Dissertation

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Diese Arbeit wurde von der TU Wien im Rahmen der Ausschreibung „Innovative Projekete – Personal“ unterstützt.

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Unterschrift

Content

Danksagung

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для Катюші

Abstract

Polypropylene (PP) with a share of 19.2% on European plastic demand is the second most important commodity polymer. Nearly half of the produced PP ends up after a short period of use as post-consumer waste. Recycling rates of PP are increasing since years, but converting PP-waste into a valuable resource is still a challenge and needs scientific research from a different perspective.

Long chain branching (LCB) is known as a suitable method to introduce strain-hardening behaviour to virgin polypropylene and increases thereby the melt strength. Commonly, thermo-oxidative degradation, ageing and shear induced chain scission during recycling reduces viscosity and molar mass. As a result, most of recycled PP is a product of worse quality compared to virgin material, thus this process can be regarded as "down-cycling". LCB is shown as an innovative tool for value adding to PP from household post-consumer waste, therefore, one can speak of a real “up-cycling”.

Within this study, we first investigated the influence of polymeric impurities like polyethylene with high density (PE-HD). Model mixtures from PP containing 10% PE-HD were prepared, chemically modified and compared with pristine PP. The same study was repeated with post-consumer material from household plastic waste. The melt properties were improved in any case, independent on the PE-HD in the blend. However, the mechanical properties showed mixed results, especially in the case of the post-consumer feedstock, the material suffered from the formation of highly branched gel particles and an unfavourable viscosity ratio of the PE-HD impurities.

However, single polymer PP post-consumer waste did not show any limitation, so the investigation was continued on the influence of different linear PP-grades and therefore different molar masses (but similar molar mass distributions) on the LCB formation itself. The branching number – for the comparison of the number of LCB per molecule – was determined by high temperature size exclusion chromatography and dynamic rheology. PP-types with higher molar masses, like for pipe extrusion, show lower number of LCB per polymer chain compared to an injection moulding PP-type with low molar mass under the same conditions for the LCB-reaction. The higher viscosity (caused by a more entangled structure), caused by the higher molar mass inhibits the

migration of the chain fragments through the polymer melt and reduces the efficiency of the branching reaction.

Due to the promising results from the experiments in the laboratory scale twin-screw-extruder (gram scale), a scale-up to a bigger single-screw extruder was performed. For this the reaction parameters need to be modified for the changed processing parameters (shorter dwell time). The single-screw extruder not only gave more up-cycled PP in shorter time, also the shear stress on the polymer was less pronounced, therefore the results were better, compared to the twin-screw lab extruder.

As a possible application for the up-cycled PP foaming experiments were performed in laboratory scale with $scCO_2$ in a high pressure autoclave. The up-cycled extrusion grade PP gave the best results, the cell structure was comparable to the foam of commercial foaming-type PP produced under similar conditions.

Kurzfassung

Mit 19.2% Anteil am Europäischen Kunststoffverbrauch ist Polypropylen (PP) der zweitwichtigste Kunststoff überhaupt. Fast die Hälfte des produzierten PP wird für Wegwerf-Konsumgüter und damit für einen Einmalgebrauch verwendet. Die Recyclingquoten steigen in Europa seit Jahren, aber für PP Nachgebrauchsabfall existieren erst wenige Technologien. Dies soll mit diesem Projekt geändert werden.

Langkettenverzweigung ist eine gängige Methode, um die Schmelzesteifigkeit von PP durch dehnverfestigendes Schmelzeverhalten zu erhöhen. Während des mechanischen Recyclings kommt es zu thermisch-oxidativem und scher-induziertem Kettenabbau und dadurch zu einem signifikanten Molmassen- und Viskositätsverlust. Man spricht normalerweise von „down-cycling“. Durch die Modifikation der Struktur des Polypropylens mittels Einführung langer PP-Seitenketten kann der Verlust der mechanischen Eigenschaften nicht nur kompensiert sondern das Eigenschaftsspektrum des PP sogar noch erweitert werden. Dadurch wird ein echtes Upcycling realisiert.

Nachgebrauchs-PP stellt keine homogene Fraktion mit konstanter Zusammensetzung dar, deswegen wurde zuerst mit Modellmischungen der Einfluss vom Polyethylen mit hoher Dichte (PE-HD) – einem Fremdkunststoff – auf die Modifikation bestimmt. Unabhängig vom PE-HD wurden die Schmelzeeigenschaften verbessert, weswegen der Prozess mit gesammeltem und mit PE-HD verunreinigtem PP-Nachgebrauchsabfall wiederholt wurde. Speziell beim Nachgebrauchsabfall fielen die hohen Viskositätsunterschiede von PE-HD und PP ins Gewicht und führten zusätzlich zur Vernetzungsreaktion des PE-HD zu einer Verschlechterung der mechanischen Eigenschaften. Sortenreiner PP-Nachgebrauchsabfall stellte hingegen keine Limitierungen dar, weswegen der Einfluss homogener Verunreinigungen (PPs mit unterschiedlicher Molmasse) untersucht wurde. Die Anzahl der Langkettenverzweigungen wurde mittels Hochtemperatur Gelpermeations-chromatographie und aus den Messungen der dynamischen Viskosität bestimmt. Die ermittelten Werte wurden miteinander verglichen. Dabei stelle sich eine höhere Effizienz der Verzweigungsreaktionen bei einer PP-Type mit niedriger Viskosität (Spritzguss) heraus, im Vergleich zu einer Extrusions-PP-Type für Rohre. Die stärker verschlaufte Kettenstruktur bei den Sorten mit hoher Viskosität und hoher Molmasse

behindert die Wanderung der Kettenfragmente und reduziert dadurch die Rekombination und führt zu stärkerem Kettenabbau.

Da die Laborversuche (g-Maßstab) im 2-Schnecken-Extruder sehr vielversprechend waren, wurden diese an einem größeren 1-Schnecken-Extruder (Durchsatz im kg Bereich) wiederholt. Dafür mussten einige Reaktionsparameter verändert werden, da die Verweilzeit im 1-Schnecken-Extruder viel kürzer ist. Neben dem Vorteil eines viel größeren Durchsatze, war auch das allgemeine Viskositätsniveau der Proben höher, da im 1-Schnecken-Extruder weniger scherinduzierte Schädigung der Schmelze stattfand.

Kunststoffschäume sind ein mögliches Anwendungsgebiet für die hergestellten Up-Zyklate. Dafür wurden einige Vorversuche in einem Laborautoklav mit überkritischem CO_2 durchgeführt. Die Rohrextrusions-PP-Type mit hoher Molmasse lieferte nach dem Langkettenverzweigen Produkte, deren Schaumstruktur mit einer kommerziellen Schaumtype vergleichbar ist. Das Prozessfenster ist aber bei der kommerziellen Type um einiges größer, wohingegen beim Up-Zyklat nur unter optimalen Bedingungen ein gutes Ergebnis resultierte.

List of included publications

I. Kamleitner, F.; Duscher, B.; Koch, T.; Knaus, S.; Archodoulaki, V. M., Upcycling of polypropylene—the influence of polyethylene impurities. *Polymer Engineering & Science* **2017**, (early view) , DOI: 10.1002/pen.24522

II. Kamleitner, F.; Duscher, B.; Koch, T.; Knaus, S.; Archodoulaki, V. M., Long chain branching as an innovative up-cycling process of polypropylene post-consumer waste – possibilities and limitations. *Waste Management* **2017**, 68, pages 32-37, DOI: 10.1016/j.wasman.2017.07.022

III. Kamleitner, F.; Duscher, B.; Koch, T.; Knaus, S.; Schmid, K.; Archodoulaki, V. M., Influence of the molar mass on the long chain branching of polypropylene. *Polymers* **2017**, 9(9), DOI: 10.3390/polym9090442

List of abbreviations

ASTM	American Society for Testing and Materials
DIN	Deutsche Industrienorm
PE-LD	Polyethylene with low density
PE-HD	Polyethylene with high density
PP	Isotactic polypropylene
LCB	Long chain branching, Long chain branches, Long chain branched
PODIC	Peroxydicarbonate
DSC	Differential Scanning Calorimetry
TGA	Thermal gravimetric analysis
DMA	Dynamic mechanical analysis
SER	Sentmanat Extensional Rheometer
SEM	scanning electron microscope
HT-SEC	high temperature size exclusion chromatography
MMD	molar mass distribution
M_w	weight average molar mass
M_n	number average molar mass
MFR	Melt flow ratio
T_g	glass transition temperature
T_m	melting temperature
T_c	crystallisation temperature
η^0	zero shear viscosity
$\|\eta^*\|$	absolute complex viscosity
ω	angular frequency
$G'\&G''$	storage and loss modulus
LVE	Linear viscoelastic envelope

1. Introduction

1.1. Aim of the work

The demand and use of polypropylene (PP) is increasing and post-consumer waste is a constantly growing concern. Methods need to be adapted consistently in order to meet new requirements. The reintroduction of used PP in product loops should be the preferred option, the recovery of the energy that is stored chemically should be the very last resort. However, recycling of PP post-consumer requires reliable separation from impurities, which unfortunately turns out as quite cost intensive.

In this work, re-extrusion should meet a chemical induced structural modification of polypropylene in order to obtain a new method in waste management creating an “up-cycling” process. Little changes in molecular structure result in pronounced changes in rheological, mechanical and thermal properties. Long-chain branches should be introduced by melt free radical grafting in the structure of the linear polypropylene backbone of post-consumer PP-waste.

As post-consumer waste is highly contaminated, the influence of impurities on modification and the long-chain branched (LCB) structure, on its properties in melt and solid state is of particular importance. Especially heterogeneous impurities like 10% polyethylene with high density (PE-HD) are of special interest in this work, but also homogeneous impurities like different PP types. Oscillatory and extensional rheology are all-round tools in order to characterise the topology of LCB-structure.

The performance of modification should be tested by implementing common applications such as foaming. In combination with mechanical material testing, thermal analysis, microscopy and spectroscopy an overall picture should be obtained from the melt up to the final product.

The goals for this research and the related publications are listed as follows

- Implement a promising method for LCB of PP, that fulfil the criteria of being used in an extruder and also offers the possibility to be introduced to a real industrial process (**Publication I**)

- Verification of the LCB by dynamic and extensional rheology (**Publication I**)
- Study of the influence of impurities, which occur in PP post-consumer waste. PE-HD as the most likely impurity was added with an amount by weight of 10% (**Publication I**)
- Applying the “up-cycling”-method of LCB to a real system of PP-post consumer waste from packaging material containing PE-HD impurities **(Publication II)**
- Critical reflection and discussion of the obtained results. (**Publication I and II**)
- Summarising the influence and limitation of nature and quantity of common solid-plastics waste impurities on the chemical modification process, the processability, and the properties of application of *upcycled* PP (**Publication II**)
- LCB of PP single polymer waste and investigation of suitable PP fractions for highly efficient LCB **(Publication II and III)**
- Study of influence of the polymer structure on the chemical modification, especially by means of different PP types categorised by their molar mass **(Publication III)**
- Adjustment of the reaction parameters from laboratory extruder (g-scale) to a single screw extruder (kg-scale) for scale-up (**unpublished**)
- Investigation of the influence of the extruder geometry on the LCB by comparison of the rheological data (**unpublished**)
- Application of a physical foaming procedure in a high pressure reactor for the “up-cycled” polymers (**unpublished**)
- Relationship between rheological parameters and the resulting foams (**unpublished**)

2. Literature Review

2.1. Plastics in general

The plastics industry has developed considerably since the invention of various routes for the production of polymers from petrochemical sources more than 100 years ago. The history ranges from the first consumer plastic Bakelit®, which was introduced to the market at the beginning of the 20th century, over polystyrene (1930s), polyamide (PA 6.6 "Nylon" in 1935) and finally the polyolefins at the beginning of the 1950s. Plastics have substantial benefits in terms of their low weight, their cheap and environmental friendly production, their processability and lower costs relative to many other material types. The global production increased from 1.5 million tons in 1950 [1] to 322 million tons in 2015 [2]. Only in Europe, which represents 18.5% of the global plastic production, 60 000 plastics producers and processors had a turnover of 340 billion € in 2016 and employed 1.5 million people [2]. The history of plastics is one of the most successful in science and it is continuing. During the last years, global plastic consumption has grown consistently by an average annual rate of 5% and this rate is estimated to continue the following years. This rate is superior to other materials, like steel or aluminium. Scientists predict a global plastic demand of 400 M tons in 2020 [1]. Plastics became ubiquitous across almost all fields of economy. The profile of possible applications is still expanding and plastics delivered many benefits for the world society. For example, plastic packaged food lasts longer and reduces food wastage and plastic pipes facilitates clean drinking water for billions of humans. However, the global plastic production has been changing over the last years and China became the largest producer of plastic materials. Its global share in 2006 was about 14.5% [3] and increased to 27.8% in 2015 [2], which is illustrated in Figure 1. This trend will continue the next years and due to predicted annual growth rates of 8.5%, the key role of China will become more and more outstanding.

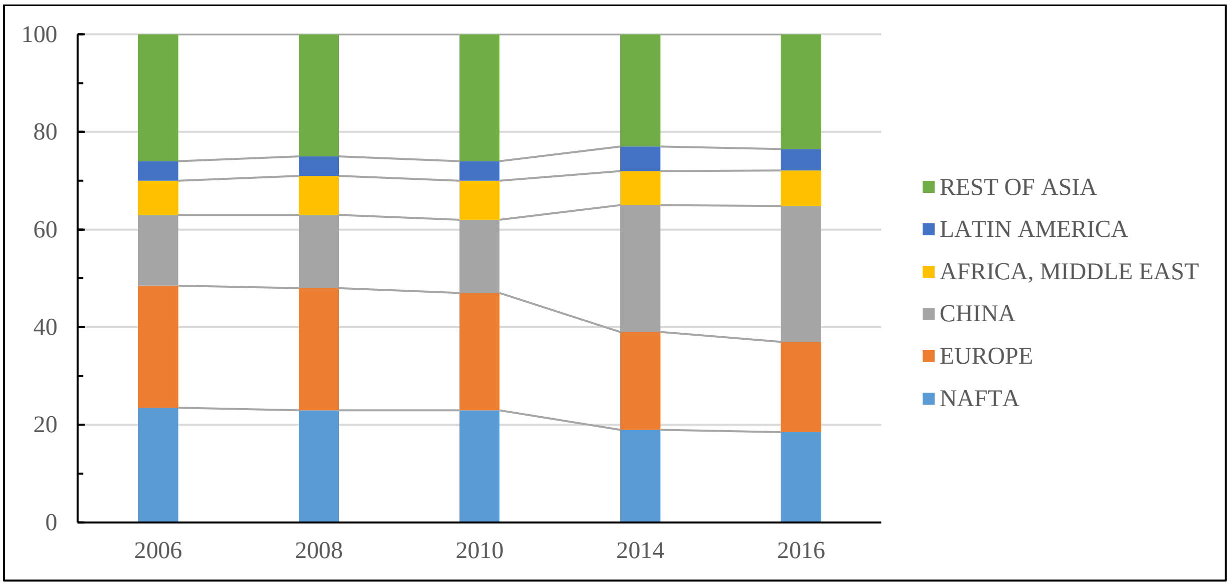

Figure 1: Global share of plastic production by region [2, 3, 4, 5, 6]

Plastic meets the needs of a wide variety of markets and became part of numerous demands of our daily life. The biggest segment in European plastic demands is packaging with a share of nearly 40% of the annual total amount of 49 million tons of plastics in 2015 [2]. But also building and construction like insulation for cables and pipe systems, as well as the automotive sector are important fields of application where plastics are used. Smaller fields are the electronic and agricultural sector, but plastics are also consumed in the sports and leisure field, furniture production and in numerous medical devices (Figure 2) [2].

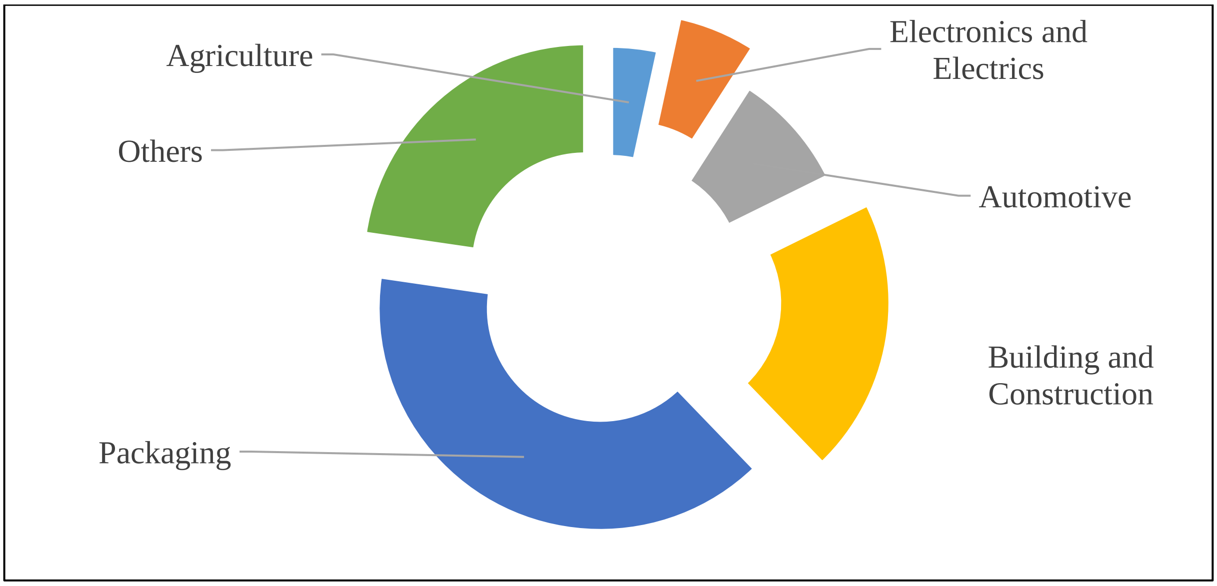

Figure 2: Application fields of plastics in Europe in 2015 [2]

Only six polymers represent 80% of the European demand of plastic, which is shown in Figure 3. Within these six polymers the commodity polymer with the largest share on European plastic demand is polyethylene (PE) with 29.4% followed by polypropylene with 19.1% [2].

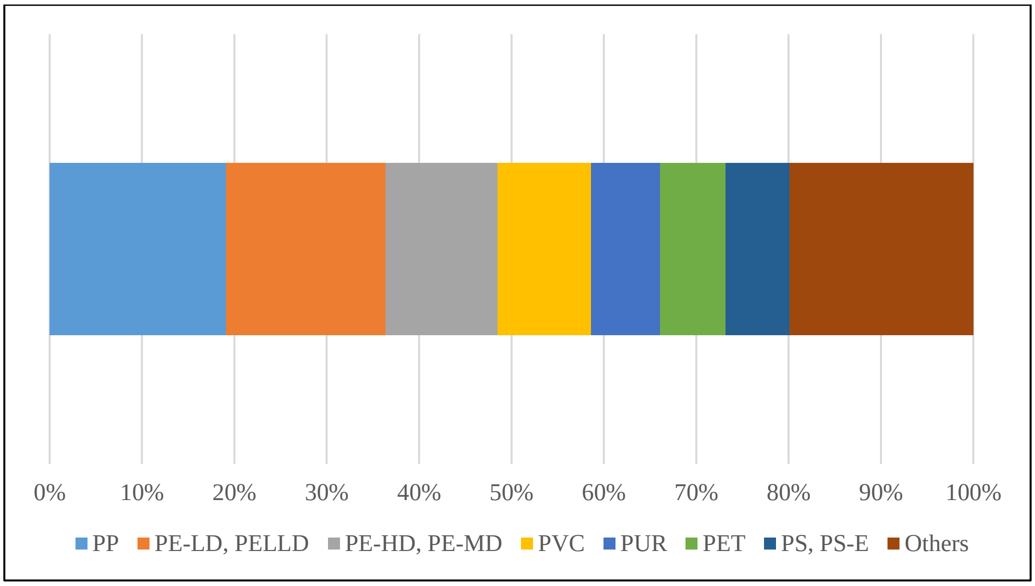

Figure 3: European plastics demand by polymer in 2015(fibres are not included) [2]

If PE is separated in its two big groups – PE with low-density (PE-LD and PE-LLD) and PE with high and medium density (PE-HD and PE-MD) – polypropylene becomes the most important plastic with 19.1% share in European plastics demand. PP and PE together represent nearly half of the total plastic demand in Europe and also worldwide [2].

Each polymer offers its specific set of benefits for numerous fields of applications in our daily life. Beside polymer specific properties (flame retardance of PVC, translucence of PS,…) the high level of technology and the utilisation of additives provide tailor-made solutions for each purpose. Figure 4 combines the statistical data from Figure 2 and Figure 3 and visualises the amount of the different plastics in terms of their application field. Therefore it can be seen, that no field exist where only one commodity plastic is used.

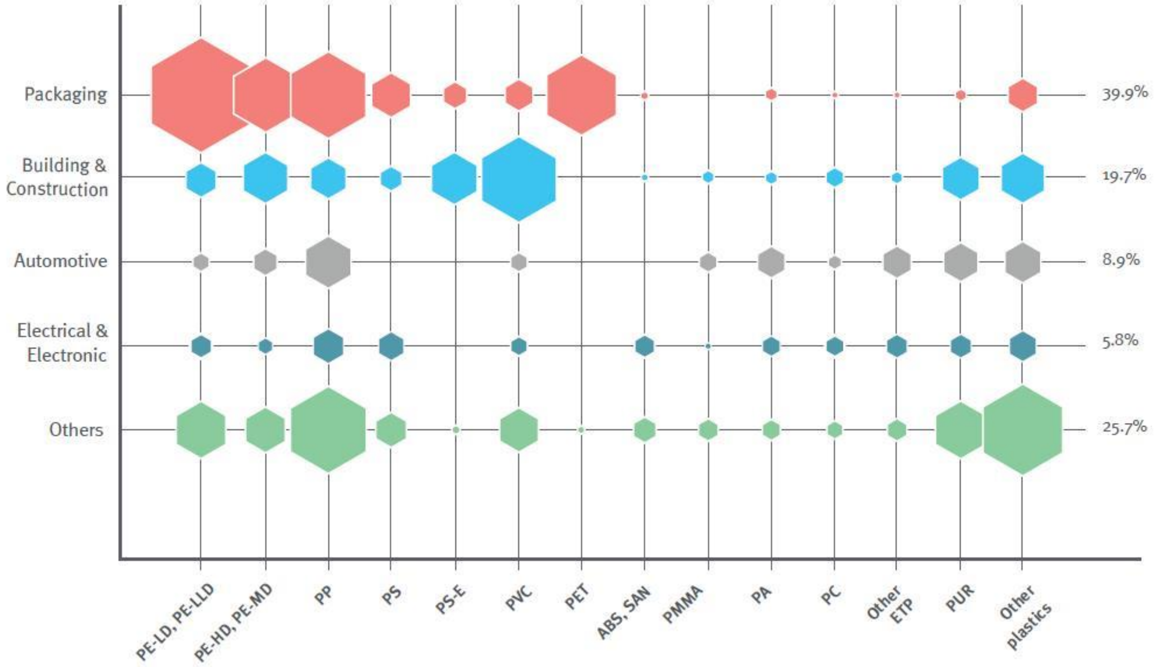

Figure 4: Plastics demand by polymer and market segment (fibres are excluded) in 2015 [2]

Plastics derive almost completely from petrochemicals produced from fossil resources like oil and gas. Around 4% of world oil and gas production is used as feedstock for plastics and further 4% to provide energy for their production. The use of renewable resources is limited. The use of bioethanol-based ethylene or methane as precursor for polymers for example can help to substitute fossil resources and can capture carbon dioxide from the atmosphere. Actually they hold a tiny fraction of the total global plastic market (less than 1%) and in many cases will have the pale taste to be in competition with food production [7, 8, 9]. Additionally, approximately 50% of the items produced of plastics are only for a short time and single-use disposable application (packaging, agricultural film, etc.) and further 20% are used for long-term single-use disposable goods like cable coatings and pipes. After more than 60 years, since the commercial mass production of polyolefin started, the current level of usage and disposal of plastics generated several environmental problems of big concern. Anyway, it is not possible to just ban plastics and plastics production. Theoretically, it is reasonable to substitute plastics exemplarily in all consumer goods. But a recent study of the American Chemistry Council showed, that the substitution of plastics by tin, aluminium, glass and paper would increase the environmental costs by a factor of more than 3.8. This primarily affects the CO_2 emission, thus plastics are also part of a sustainable economy [10].

2.2. End of life treatment of plastics

Due to their mass production, their cheap price, their limited ability to be reprocessed and the purpose of single-use applications, end of life management of plastics has become a crucial challenge for societies. Unfortunately, most plastics are not biodegradable [11]. However, UV light, oxygen, temperature and other physical and chemical factors result in a significant degradation [12]. A simple reuse by melting and reprocessing like it is common for metals and glass is not possible or at least limited in most cases for plastics. As a result, the common treatment for plastics waste was burying them in landfills. With more and more plastics products, being disposed soon after their purchase, the landfill space required by plastics waste is a growing concern. Though a well-managed landfill site results in limited environmental harm (if transport und collection are neglected), however, there are long term risks of contamination of soil and groundwater. Especially non-polymeric additives (chemicals that are necessary for production or stabilisation) in plastics and their breakdown products have to be considered. Many of these have not undergone an environmental risk assessment and their impact on human health and the environment is currently uncertain, especially when they are accumulated in big landfill facilities [13]. For example, Bisphenol-A, a breakdown product from polycarbonates or epoxy resins, was recently added to the candidate list of substances with very high concern (SVHC) according to article 57(c) of REACH (European Regulation concerning Registration, Evaluation, Authorisation and Restriction of Chemicals). However, there is no implications of SVHC identification expected for vast majority of BPA-applications itself [14]. Sure, the situation for polycarbonates and epoxy resins is not so serious because of the small share on plastic market, but polyvinylchloride e.g. – with a share of more than 10% – needs plasticisers with similar classification according to REACH. In 2014, landfilling was still the 1st option for the end of life treatment in many countries in Europe [15]. The European Commission adopted an ambitious Package for Circular Economy, which includes some legislative proposals on waste management within the European Union. The key elements of the proposal include [16]:

- A **target for recycling 65% of municipal waste** by 2030;
- A **target for recycling 75% of packaging waste** by 2030;
- A binding to **reduce landfill to maximum of 10% of municipal waste** by 2030;
- A **ban on landfilling** of separately collected waste;
- Promotion of economic instruments to **discourage landfilling**;
- Concrete measures to **promote re-use and stimulate industrial symbiosis** – turning one industry's by-product into another industry's raw material;
- Economic incentives for producers to put **greener products on the market** and support recovery and recycling schemes

Countries like Switzerland, Austria, Netherlands, Germany, Sweden, Luxembourg, Denmark, Belgium and Norway already banned landfill and achieve very high recycling rates (up to 99% and higher). But also in other countries of the European Union (EU) recycling rates are increasing since the last years and the amount of plastics waste, which goes to landfill decreases. The trend can be seen in Figure 5 for the EU27, Norway and Switzerland [2].

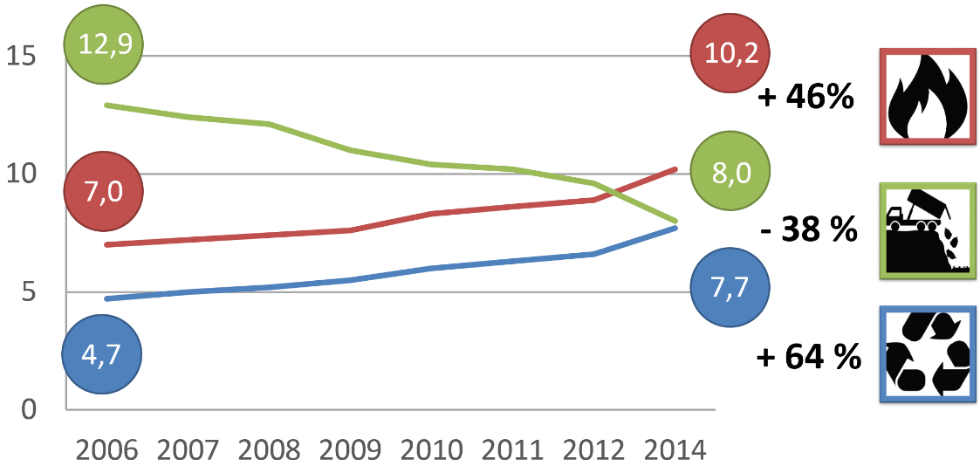

Figure 5: Plastics waste treatment in EU 27 + NOR and CH in million tons 2006-2014. [2, 3, 4, 5, 6, 17]

Incineration of plastic waste to recover the energy that is saved in the carbon bonds became the preferred method for the treatment of municipal solid waste. There is no need for sorting and the building of special facilities for the burning of waste is less sophisticated than other technologies. So this trend, which is shown in Figure 5, is expected to continue the next years [2]. Energy recovery by incineration reduces the need for landfill of plastics waste, but there are concerns about hazardous substances may be released into the environment during this process. Especially PVC and halogenated additives (e.g. flame retardants) that are part of typical mixed plastics waste are of major concern. These impurities lead to the risk to release hydrochloric- or hydrobromic acid, or in worst-case dioxins or other polychlorinated biphenyls in the atmosphere [18]. As a consequence a sustainable waste management strategy is necessary for dealing with mixed municipal solid waste and the quality of incineration itself has to be good enough [19]. Then incineration turns out as a valuable key in a sustainable circular economy of plastics. However, burning of plastics for energy recovery is not the most suitable option, recycling should be preferred for plastics waste [2].

Recycling has to be separated in four different groups according to ASTM D5033 [20]. The so-called primary recycling is the re-introduction of single-polymer waste material to the extrusion cycle to manufacture products of the same quality. Nowadays it mainly takes place in internal waste management of plastic processors. Secondary recycling is the process to recover plastics waste from external sources for the re-use in manufacturing plastics products by mechanical means. Mechanical recycling, another term for primary and secondary recycling according to ISO 15270 [21], in most cases can only be performed with single-polymer plastics. Plastics tend to be not very miscible with each other, due to differences in their chemical composition. Phase separation occurs, which leads to a deterioration of the mechanical properties. Separation, sorting and washing are essential steps to produce a product of high quality. A possibility to tackle commingled plastics waste is chemical or tertiary recycling. This is a collective term for advanced processes to depolymerise plastics waste to recover base chemicals for the chemical industry. Quaternary recycling or energy recovery has already been discussed above [22, 23, 24]. The four recycling routes discussed related to the production cycle of polymers are shown in Figure 6.

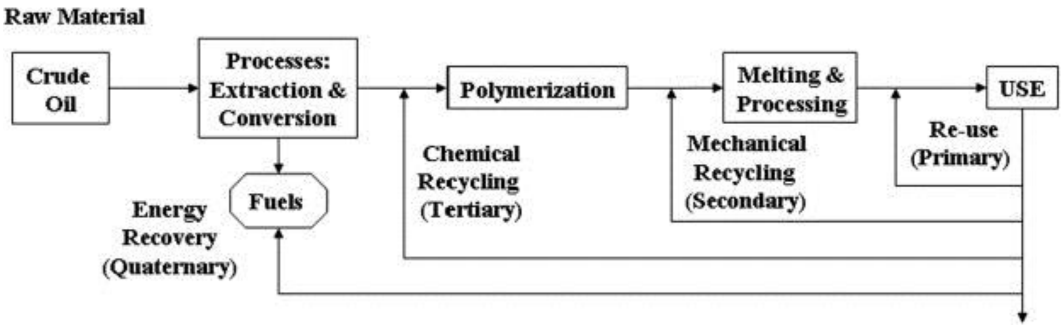

Figure 6: Recycling methods related to production cycle of polymers [25]

Except burying them in landfill, there is no general waste treatment concept that fits to all plastics. Every recycling concept has to be tailor made for a single polymer waste fraction to get a product of a quality capable to compete with the equivalent virgin polymer. The recycling of thermosets for example is limited to grinding and incorporation into an uncured monomer mixture as a filler. Thermoplastics, that can be heated and remoulded, offer a broader variety for recycling, which is also still limited because of numerous difficulties. Only poly-ethylene-terephthalate (PET) has already reached a high standard of recycling.

PET is used for beverage bottles and was down-cycled to produce textile fibres in former recycling processes, but the last years brought superior recycling processes (e.g. PET-to-PET GmbH in Austria) [26]. Within this process there are two crucial steps. First, the shredded PET-flakes are etched with a solvent to get clean surfaces and to remove impurities to fulfil the high hygienic standard for beverage bottles. Second, the molar mass is increased during re-extrusion by using residual catalyst in the material for re-condensation reaction, to compensate partial hydrolysis from product life. Therefore, PET recycling can reach the high technological state of a so-called closed loop recycling [27, 28].

Polyolefins, however, do not offer this opportunity:

Polystyrene (PS) for example, is used in solid non foam products or in expanded foams. PS has its biggest scope of application in food packaging where high hygienic standards make it nearly impossible to simple reintroduce recycled PS from post-consumer waste. Due to its chemical nature, some special recycling concepts exist for PS. Unlike other polyolefins PS is soluble in organic solvents, e.g. acetone. The production of a jelly-like polymer solution reduces density, makes it easier for transportation, and offers the possibility to remove solid and non-soluble impurities. PS also offers the opportunity of depolymerisation (feedstock recycling) to produce styrene monomer to form new PS of the same quality. Both processes are highly energy consuming, as a result, the amount of recycled PS is still below the expectations [29, 30].

PE, the plastic with the biggest share on global market, provides totally different requirements for recycling. If properly sorted the material can be recycled together with virgin material. This was shown by Pattanakul et al. who prepared a recycled PE-HD with different contents of virgin PE-HD material and recycled PE-HD from milk bottles [31]. However, Loultcheva et al. used PE-HD from containers for liquids for recycling and showed a dependency of the reprocessing conditions on the mechanical properties [32]. Boldizar et al. and Kartalis et al. studied the influence of reprocessing and accelerated thermal ageing on PE-HD from recycled bottle waste. The ageing reaction depends on the used polymerisation catalyst. According to Moss and Zweifel unstabilised Phillips-PE undergoes cross-linking and Ziegler-Natta-PE chain scission [33] as well as metallocene-PE, which was shown by Hoáng et al. [34]. PE-HD undergoes crosslinking during ageing which influences the mechanical properties. The addition of re-stabilisers reduces the negative side effects of ageing [35, 36]. However, the use of a recycled PE resin of different origin may not ensure that all of the narrow processing specifications can be met. Due to the fact that more than 100 grades of PEs exist, it is impossible to meet the exact specification required. To generate a single polymer fraction, which is required for mechanical recycling Pappa et al. presented the selective dissolution/precipitation technique for the treatment of mixed polyolefin waste to get pure PE and PP fractions [37]. Thus, it is possible to generate a single polymer fraction from a mixed fraction [38, 39, 40]. To avoid cost intensive sorting another concept for the recycling of mixed polyolefin waste is offered by tertiary recycling. Especially PE offer the possibility of pyrolysis to generate crude oil-like products for petrochemical applications or liquid fuels [41, 42].

2.3. Recycling of polypropylene

2.3.1. Polypropylene in general – synthesis and general properties

After the aforementioned PE, PP is the polymer with the second biggest share on global plastic market with about 20%. The monomer propylene derives from steam cracking process of naphtha. During the radical polymerisation the configuration of the monomer in the polymer can change. This phenomenon is called tacticity (Figure 7). A simple radical polymerisation, similar to the high pressure tube reactor process of PE-LD, results in atactic PP homopolymer. The methyl-group is randomly located across the polymer chain. The mechanical performance is very weak and its application window is very small.

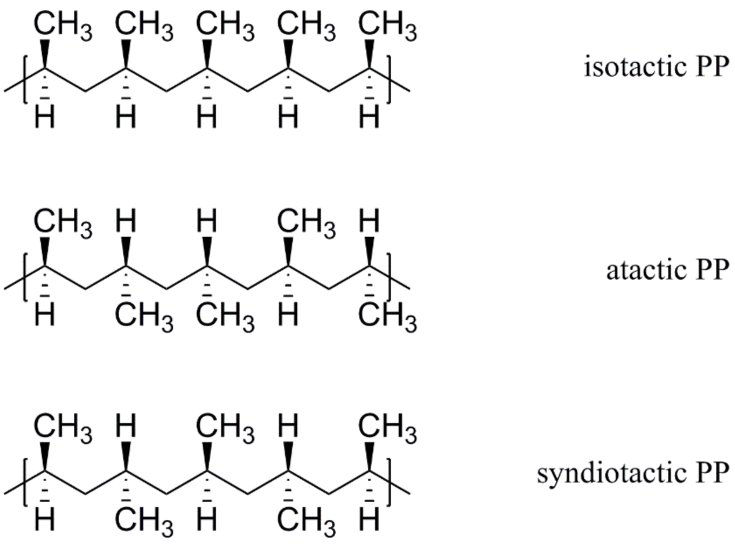

Figure 7: Different configurations of PP

The group of Giulio Natta synthesised isotactic PP from propylene monomer first, when they used a catalyst developed by the group of Karl Ziegler for the polymerisation of ethylene. This process – now called Ziegler-Natta – made it possible to produce PP with high isotacticity. The mechanism of the polymerisation reaction can be defined as an insertion of olefin units to a transition metal salt and a main group alkyl metal, which acts as activator and serves for the purpose to generate the active metal-carbon bond. The formation of the active catalyst is shown in Figure 8 with titanium tetrachloride and triethyl aluminium.

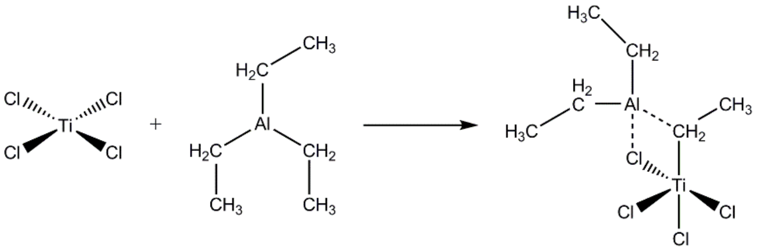

Figure 8: Formation of the active Ziegler Natta catalyst from titanium tetrachloride and trietyhl aluminium

In the next step (Figure 9), the double bond of the olefin coordinates to the transition metal centre which activates the double bond (I). The α-carbon bonds to the titanium and the β-carbon to the alkyl of the alkylaluminium (II). The monomer gets inserted between the alkyl of the trialkylaluminium and the titanium metal. Consequently, the former α-carbon gets activated by the aluminium and the reaction continues with the next monomer (III).

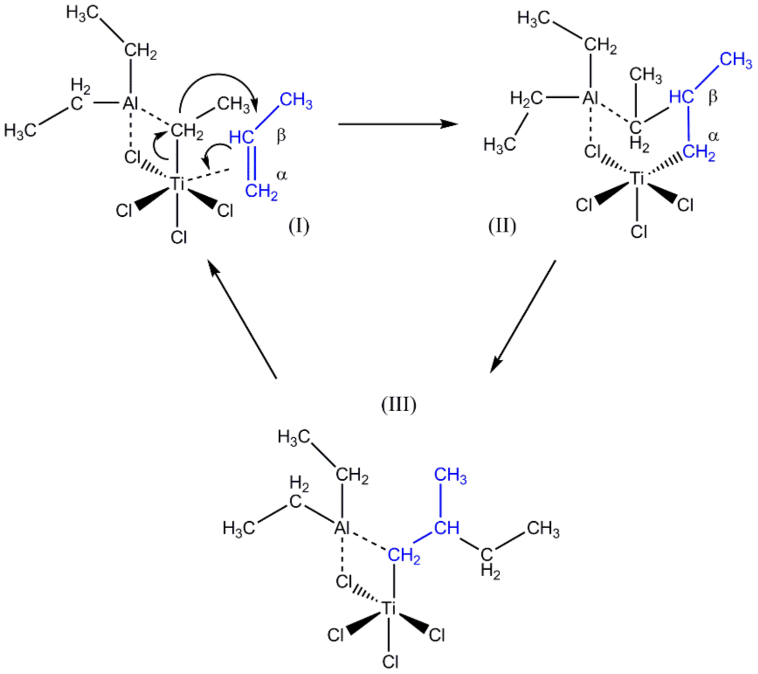

Figure 9: Propylene insertion polmyerisation with $TiCl_4$ and Et_3Al

The first generation of Ziegler-Natta catalysts was introduced to industry in 1954. Their productivity was 2-4 kg PP per g of catalyst, the isotacticity index was between 90% and 94%. PP was produced in so called slurry processes, where the catalyst is dissolved in a suitable solvent that also offers high solubility for the gaseous monomer. Catalysts of the 5th generation, which were introduced to the market in 1988, had already a productivity of more than 100kg PP per g catalyst, higher isotacticity and gave the possibility of tailor-made polydispersity [43]. Due to the high energy costs for the separation of the solvent and the drying of the polymer, modern polymerisation processes are carried out in bulk and gaseous phase. The catalyst is a highly porous solid substrate that enables the high productivity. The resulting reactor grade PP powder gets pelletised, stabilised and is ready for selling. Novel processes like the Borstar™ process (Figure 10) allow a full range of PP grades ranging from high MFI PP for injection moulding to low MFI for pipe extrusion. The monomer is loaded with catalyst and pre-reacted in the loop-reactor (a and b in Figure 10) under supercritical conditions. The propylene is solvent and reagent in one. The slurry is transferred in several gas phase reactors and the reaction is continued under different pressures and temperatures (c, d, and e in Figure 10). Unreacted propylene gas can be recovered and reinserted to the process. High market pressure and years of innovation made the processes to produce PP to the cleanest, most cost effective and most efficient ones in chemical industry [1, 44, 45].

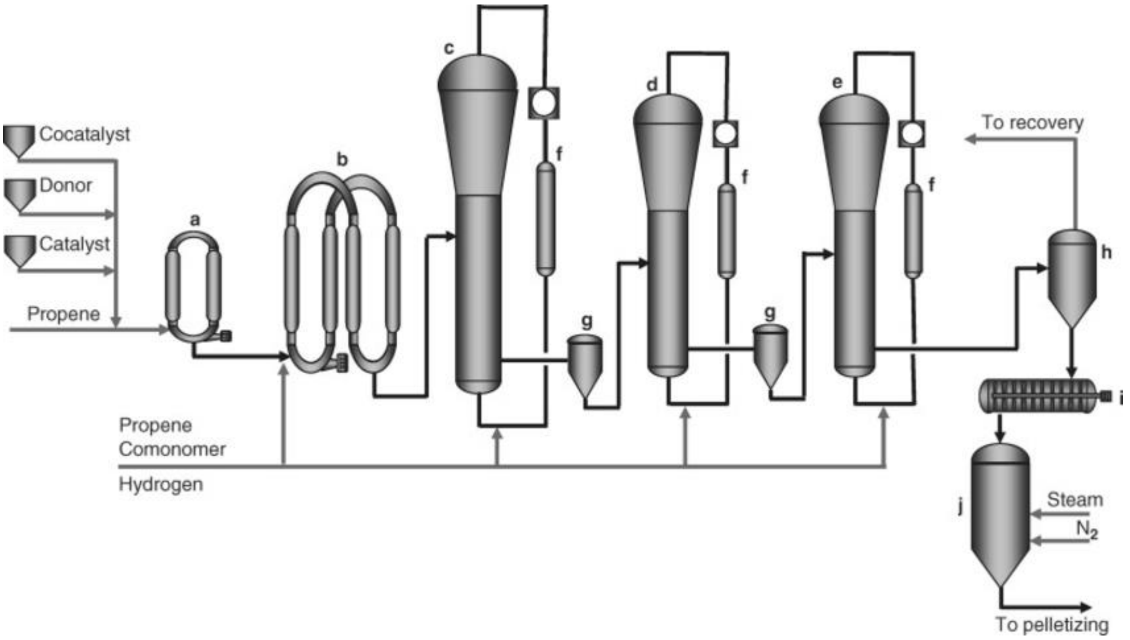

Figure 10: Process scheme of the Borstar™ process by Borealis [45]

Three types of PP are available on the market:

Isotactic linear PP homopolymer can be defined as the standard resin (94% of PP homopolymer), whereas the amount of atactic or syndiotactic PP can be neglected. PP has a low impact resistance, consequently impact modification has become a special field of interest since the introduction to the market.

As a result, copolymers of ethylene and propylene were produced. Impact PP-copolymer has the highest impact resistance and is a block-copolymer of propylene with varying amounts of ethylene.

The third type is a PP random copolymer of propylene and ethylene, which contains ethylene-propylene amorphous phases and crystalline PP segments. PP random copolymer has the highest transparency.

In addition to the three mentioned polymer types, several additives are available to expand the application field of PP. For example talcum filled and glass fibre reinforced PP to increase the rigidity and to decrease the creep.

PP homopolymer is a transparent to opaque semi crystalline polymer with a specific density of about 0.90-0.91 g/dm³. Its oxidation and UV resistance is low, thus the addition of stabilisers is necessary. Compared to PE-HD, PP outperforms with a higher melting temperature of $158°C < T_m < 167°C$, a higher hardness (shore D 70-83; PE-HD 56-71) and a higher tensile modulus (1200-2000 MPa; PE-HD 180-1800 MPa). However, the glass transition temperature is quite high and lies between $-5°C < T_g < 5°C$ [1]. PP is resistant to most of the organic and inorganic acids and bases and insoluble in common solvents. PP is only soluble in some polychlorinated hydrocarbons or high-boiling aromatics and aliphatics (e.g. xylene and decalin) [1, 43]. Contrary to PE, PP does not undergo radical induced crosslinking. The formation of a macroradical on the PP-chain is most likely on the tertiary carbon atom. Chain scission between the tertiary β-carbon, leads to a second radical and an α-olefin. This process is called β –scission and the mechanisms is shown in Figure 11 [43].

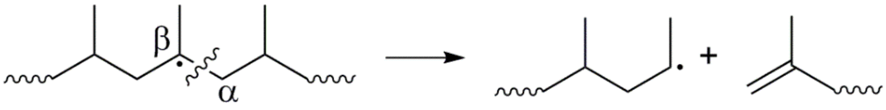

Figure 11: β-scission of PP

Beta-scission is less pronounced in the solid state and increases significantly with temperature, especially when the polymer is molten. Thus, melt modification of PP is a challenging topic in science [46].

2.3.2. Applications of PP

Due to its advantageous product properties, its cheap production and the broad window for processing, PP found its application in nearly all facets of our daily life. Its application window ranges from classical packaging (blow moulded or chill roll casted films or rigid injection moulded packaging) and consumer goods like injection moulded toys or microwave proof containers, to technical parts especially for automotive industry and pipes, but also to the production of fibres for e.g. carpets [2]. Among plastics, PP, like other polyolefins, has an extremely low environmental impact and shows a significant benefit over other materials – like glass – for food packaging [47]. Figure 12 shows the five biggest application groups of PP and its shares in European PP demand.

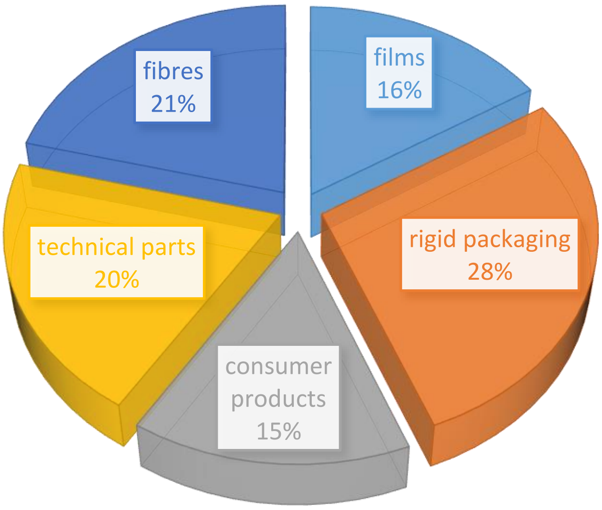

Figure 12: Applications for PP and their shares in PP demand [43]

According to [43], nearly half of the European PP demand is used for the production of packaging material, therefore only for a short time single use of the material. Other applications have longer periods of use, however, PP is not biodegradable, so there is a need to think about end of life management of PP.

2.3.3. Recycling of polypropylene – state of the art

PP is one of the most recyclable polymers, however, the economic viability of PP recycling is hindered by the low cost of the virgin polymer. The price per kg virgin PP homopolymer resin granules was about 0.70-0.75 €/kg in the first quarter of 2017. The price for recycling grade PP with high purity was 0.70 €/kg at the same time [48]. The economic constraints do not allow the recycler to perform costly recycling processes such as extended sorting or expensive additives [29]. Another problem of recycling is to ensure reliable material supply, which is more a problem of logistic rather than processing technology.

2.3.3.1. Mechanical recycling of post-industrial PP-waste – primary recycling

Big PP processors established efficient in-house – primary – recycling concepts for production scrap like sprue waste, punching, edge-trim, machine start-up scrap or reject parts. Special extrusion lines equipped with appropriate shredding devices are available for the regranulation of the in-house waste [49]. This mechanically recycled PP can be added to the virgin material without any loss of material properties. Nevertheless, the innumerable small plastic processors rather tend to dispose their waste from production, than to recycle or reuse it. However, a direct recycling "in-house" of post-industrial PP waste presents no problem, but as soon as the finished PP good leaves the factory numerous difficulties occur for the recycling of post-consumer PP waste [43, 50].

2.3.3.2. Mechanical recycling of PP post-consumer waste - Secondary recycling

PP competes with other polymers in countless applications (see Figure 4), thus there is hardly any application were only PP is used. If the properties of recycled PP are to be preserved, the PP must be sorted from other plastics from municipal or industrial post-consumer waste, or it is possible to collect single polymer PP post-consumer waste.

A well-established recycling concept is PP from end of life vehicles [51, 52]. Since the environmental legislation of the European Union requires the reduction of disposed waste (landfill) to 5% of end of life vehicles, the number of licensed dismantlers has increased. Dismantled parts (e.g. bumpers) made from PP can be collected for recycling. Recycled PP from end of life vehicles is only a side product, the main aim is the recovery of ferrous and non-ferrous metals. This can be highlighted for the recycling of car battery cases. The PP is not recycled because of its value, but economic interest for the lead and legislative pressure to prevent the lead from entering the landfill are the pushing factors for this concept [53]. After dismantling, the hulk is shredded. The residual from shredding process (about 20-25% or 2 million tons per year) contains mainly of combustible mixed plastics [54]. Although, the reintroduction of the recycled plastic to the production of new cars has a good impact on greenhouse gas emission, it is often not profitable for the companies [55]. As a result, the last years brought a rethinking in car producers to change the vehicle design to meet the needs of recycling industry. Improved understanding of recycling processes will help car designers to avoid contaminants in the recycled product and improve the efficiency of the recycling [56].

Construction waste is the second big source of single polymer waste PP. But PP also competes here with other plastics like PE and PVC [57]. This fraction consists of long-term infrastructure like pipes, cable coatings and other structural materials. Especially cable coatings and most structural materials are rarely supposed to perform at the maximum limits of PP. But for pipe systems, which are used for sewage or hot water partially degradation occurs, which has to be considered when the material is recycled [50].

Compared to plastics from municipal solid waste, there ought to be no real technical and logistical problems involved with bulky waste recycling. Items like carpets and garden furniture are a possible source for PP, which can be sorted manually from other plastics, provided that the items have a recycling code for the identification [50, 58, 59].

When mechanical recycling of municipal solid waste is discussed, sorting represents the crucial point. Sorting is the most important step in recycling of mixed plastics waste to guarantee a recycled product of high quality. In case of municipal solid waste, first, plastics have to be sorted from ferrous and non-ferrous metals, glass and paper. State-of-the-art material recovery facilities use air separation and near infrared multi sensor sorting machines [60]. A flow chart of sorting recyclables from municipal solid waste is shown in Figure 13 [61]. The sorted mixed plastic fraction (PET often has already been separated) is further sorted by sink float in water to separate PP and PE from other plastics with higher specific density.

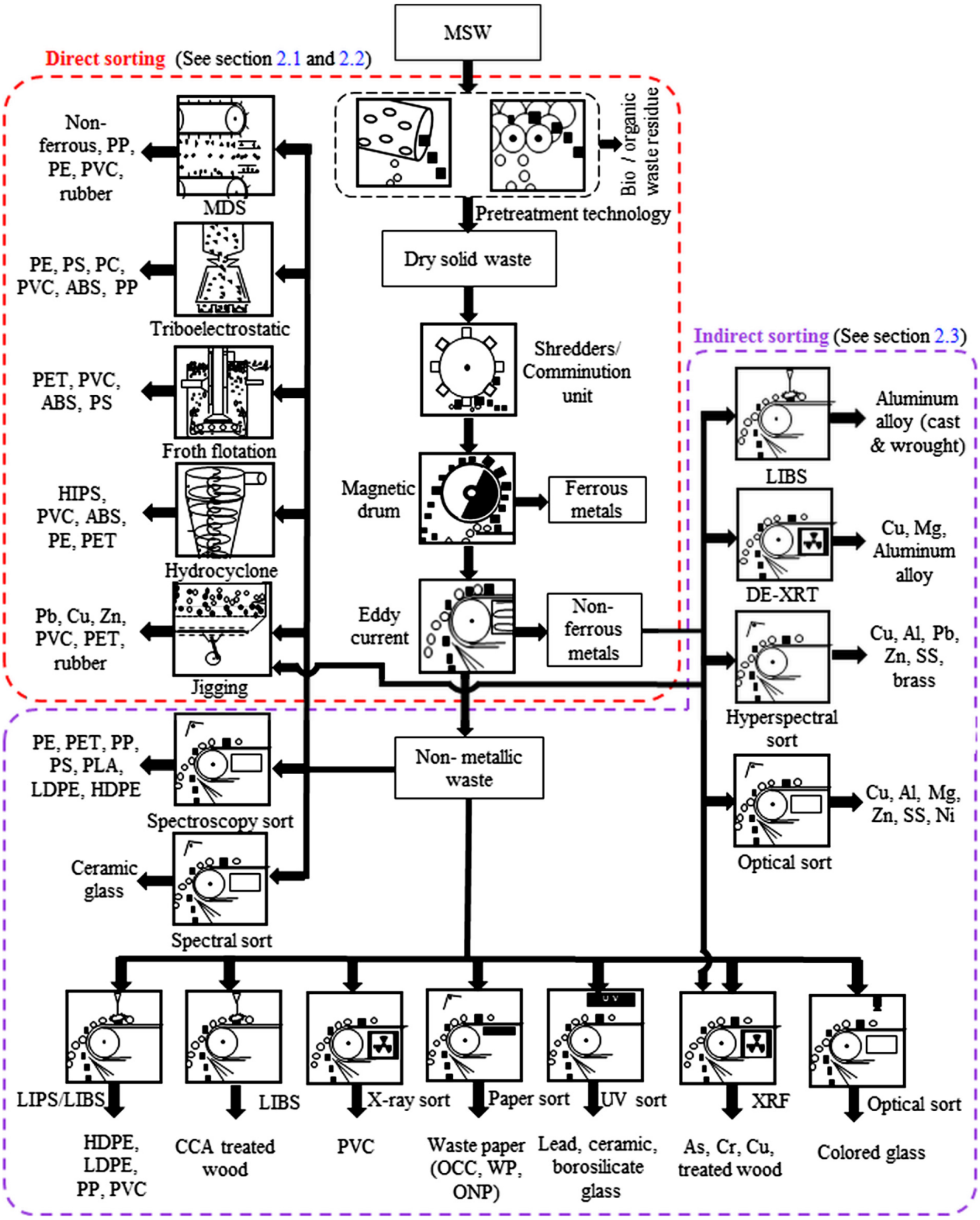

Figure 13: Flow diagram of automated sorting of municipal solid waste [61].

The composition of these PP/PE float fractions depends on the feedstock material and ranges from a PP:PE ratio of 70:30 (end of life vehicles) to 25:75 (packaging waste). To increase the grade of the polyolefin fraction over 97%, which is the requirement for high quality products, new technologies like magnetic density separation were presented by Bakker et. al. [62]. Magnetic density sorting is similar to conventional sink float, but instead of water as separation medium a liquid containing magnetic iron oxide particles in nm scale is used. Due to applying an artificial density in form of magnetic forces the effective density of the liquid varies in direction of the magnetic force and creates a medium with a density gradient. This method is applied in lab-scale and offers the possibility to get 98% PP [62] and 98.8% PE [63] grade. Another concept for the separation of the mixed polyolefin fraction is the dissolution/precipitation technique that uses xylene as solvent to dissolve the polyolefin and precipitate it with acetone. This method offers good purities of the resulting PE and PP [37, 40], but the separation of the solvent and high amounts of solvent itself are challenging.

2.3.3.3. Chemical and feedstock recycling of PP – tertiary recycling

Primary and secondary recycling are limited to thermoplastics and single polymer waste fractions. Thermochemical processes from tertiary recycling, like thermal (pyrolysis), catalytic and hydro-cracking, are able to convert mixed polymer waste into monomers, fuels or other valuable resources for petrochemistry [64]. Gasification produces synthesis gas by partial oxidation of plastics waste for other synthetic routes like Fischer-Tropsch processes [65]. Especially polyolefin waste, which contains only hydrocarbons, is a very suitable resource for such processes. The production of liquid fuel is a good alternative to use the high calorific value of around 40 MJ/kg to conserve fossil resources [66]. Commercial processes like the BP process use mixtures of naphtha with 10% PP/PE for steam cracking to produce fuel. However, only 0.03% of all generated plastics waste were chemically recycled in 2009 [41].

2.3.3.4. Quaternary recycling – incineration of plastics waste

During the last years, a number of life cycle assessments have been made comparing the end-of-life treatment of plastic post-consumer waste. According to these studies, landfilling of plastics waste proved to be the least preferred option for all considered impact categories. Furthermore, mechanical recycling is generally the environmental preferred treatment option. However, it is obvious that the virgin material substitution ratio and amount of organic contamination lead to recycling showing lower environmental benefits than incineration with energy recovery [67]. Especially for polyolefin waste containing PP, energy recovery is the preferred option because of the high calorific value of around 40 MJ/kg waste and the clean waste gas that should only contain of CO_2. Consequently, co-incineration of polyolefin waste with municipal household waste is increasingly practiced to increase the heating value and facilitate an efficient incineration to recover the energy content of other parts in municipal solid waste. For many bigger European cities (especially Vienna) this concept is the state of the art for the treatment of their municipal solid waste. However, even of the high technological level of converting waste to energy, public distrust incineration because it produces greenhouse gases and – when not properly performed – other toxic pollutants like polychlorinated compounds [68].

2.3.4. Challenges in PP recycling

The most crucial step for secondary recycling of PP is sorting to get single polymer waste, which is easier for not shredded bigger parts made of PP. Otherwise highly sophisticated sorting technologies have to be used, but give still no satisfying results for commingled polymer waste from municipal solid waste.

The question, which has to be discussed: Why does PP have to be sorted from other plastics?

2.3.4.1. *PP is not miscible with other polymers*

The state of miscibility of any mixture can be described by the free energy of mixing ΔG_{mix} given in equation 1,

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{1}$$

where ΔH_{mix} and ΔS_{mix} are the thermodynamic parameters of enthalpy and entropy change by mixing. A system is miscible when ΔG_{mix} takes negative values. Mixtures of polymers are called blends, the production thereof is called blending. Blends are classified as homogeneous (the components are miscible) or heterogeneous (the components are immiscible). Immiscible blends undergo phase separation, so homogeneous blends are also called single-phase system [69]. Miscibility in polymers has the same meaning as on low molar mass components. Alcohol and water are miscible, oil and water are not. Homogeneous polymer blends have the thermodynamic ability to be mixed at the molecular level and form miscible amorphous phases. Therefore, similar to the boiling temperature of binary fluid systems, the glass transition temperature T_g characterises pure polymers and polymer blends. T_g reflects wether a system is miscible (characterised by one T_g), partially miscible or not miscible (separated T_g), which is illustrated in Figure 14 [70].

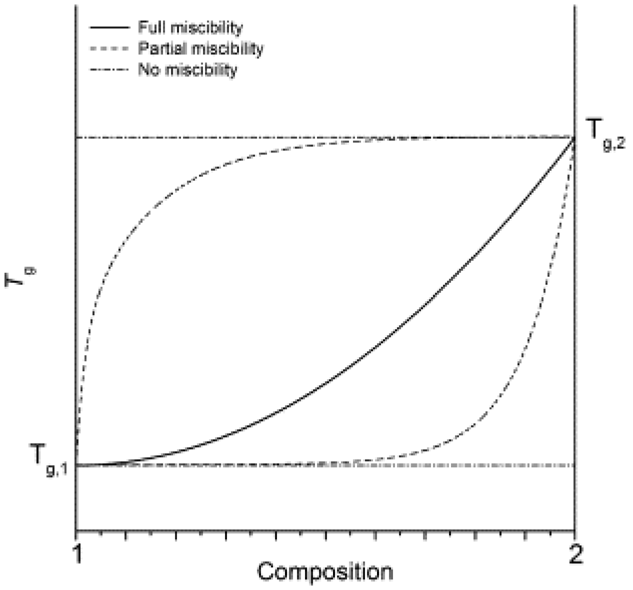

Figure 14: Dependency of Tg on the composition of a binary blend [70]

However, most polymers are not miscible because of their positive enthalpy of mixing and their small combinatorial mixing entropy [71]. At this point it has to be mentioned that the word "miscibility" and "compatibility" are not related to each other. Two immiscible polymers can be mixed and show good compatibility by means of the resulting mechanical performance.

The only PP-blends reported miscible are those with atactic PP, ethylene-propylene-rubber (EPR) with far less than 10% ethylene content and poly-1-butene [72]. The miscibility is limited to the amorphous phase and the crystalline phase is formed by neat iPP. Consequently, most multicomponent polymer systems containing PP and other commercial plastics are not miscible and therefore heterogeneous. The dispersed polymer impurities separate from the PP matrix and the resulting poor phase adhesion in solid state causes premature fracture compared to the pure matrix polymer. Figure 15 shows for example two SEM micrographs of the fracture surfaces of an unblended PP and a ternary melt blend containing PP, PE-HD (both for chill roll casting) and a standard PS resin (for thermoforming). PE-HD is finely dispersed in the PP matrix, while PS separates in spheres from PP.

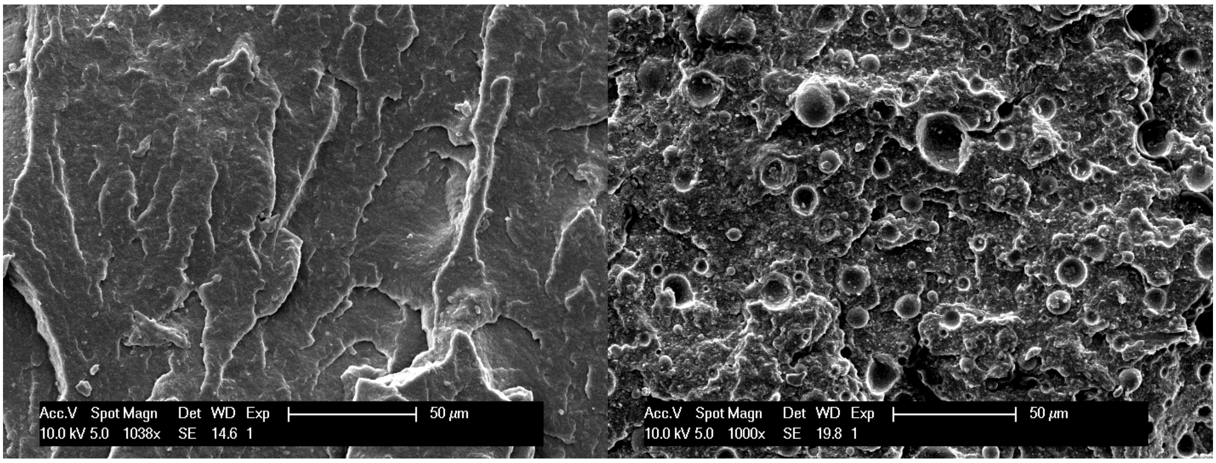

Figure 15: Comparison of unblended PP (left) and a ternary PP/PE/PS-Blend (right)

It has been reported that polymer blends need stable dispersions with small dispersed phase droplets with diameters below 0.3 µm to 3 µm [73]. It is obvious that the blend in Figure 15 does not fulfil this requirement (finely dispersed PE-HD fulfils it, but the PS spheres are about 10 µm in size) and the mechanical properties can be expected as poor relative to the neat components. The size and the shape of the dispersed phase drops mainly depends on the interfacial tension, the shear rate during processing (mixing efficiency) and the rheological properties of the components. For example, if the interfacial tension decreases the drop size diminishes. In common immiscible blends the unfavourable interactions between molecular segments lead to a large interfacial tension [74]. The interfacial tension γ_{12} of two immiscible polymers can be calculated with equation 2 according to Good and Girifalco [75].

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\varphi(\gamma_1\gamma_2)^{1/2} \tag{2}$$

The surface tensions γ_1 and γ_2 can be measured by e.g. pendant drop method and the semi-empirical interaction parameter φ, which describes the adhesion and cohesion of the two phases can be calculated according to [75]. Thus the interfacial tension decreases with similar polarities [76]. Exemplarily, the interfacial tension of a binary PP/PE-blend is 1.2 mN/m and for a PP/PS-blend 5.8 mN/m, given in [77]. This can explain the poor phase morphology of the shown PP/PE/PS-blend in Figure 15, but it is no general explanation for the poor phase morphology of common PP/PE-blends.

Wu [78] studied the formation of a dispersed drop in a matrix during melt mixing, like processing in a twin-screw extruder. In his master curve (equation 3) he describes the correlation of interfacial tension, shear rate G and the viscosities of dispersed phase η_d and matrix η_m with the diameter of the dispersed particles a.

$$\frac{G\eta_m a}{\gamma} = 4(\frac{\eta_d}{\eta_m})^{\pm 0.84} \tag{3}$$

The particle size is directly proportional to the interfacial tension and to the ± 0.84 power of the viscosity ratio between matrix and dispersed phase. Consequently, a low interfacial tension and the unity of the viscosities of dispersed phase and matrix are crucial for a small particle diameter in stable dispersion and therefore for good physical properties of the resulting blend. Coming back to the example in Figure 15, PP and PE-HD serve the same purpose (casting) and have similar viscosities contrary to PS, so PE-HD is finely dispersed in the PP-matrix and PS forms large inhomogeneous spheres.

Despite sorting of a homogeneous PP fraction without any polymeric impurities from commingled plastics waste, secondary recycling is a challenge. One recycling code signifies three types of PP (isotactic PP, PP block-CoPo and PP random-CoPo) and commercial blends and all can be filled or not filled. Furthermore, it is difficult to maintain consistent quality as each PP-type can vary strongly in its molecular properties, like the degree of branching, the molar mass, etc., and the additive composition. Consequently, PP has not only to be sorted from other plastics it also has to be sorted from itself.

2.3.4.2. Commercial PP-blends

Blending of PP with PP rubber (saturated ethylene-propylene-diene-copolymer, EPDM or ethylene-propylene random-copolymer, EPR) is a very suitable method to modify PP and is commercially used [79]. It increases the impact resistance and the elongation at break, and reduces the modulus. The properties of PP/EPDM blends are very well-studied by van der Wal et al. [80, 81, 82, 83, 84] and also PP/EPR-blends are well understood [85, 86, 87, 88, 89, 90]. PP blends are made via in-reactor blending or by post-reactor blending. The first method involves the blending of different polyolefins in a polymerisation reactor. One example is an in-reactor-made iPP/EPR blend, which is normally prepared by adding ethylene monomer to propylene monomer toward the end of propylene polymerization process [91]. The second method involves mechanical blending of a premade PP with the blend component in compounding extruders. Post-reactor blending via single and twin screw extruders is the preferred method for blending because of time, convenience and cost-efficiency [92]. Blends of PP and EPR are reported immiscible in melt at ethylene contents > 10% [72, 93, 94, 95] and in most blends, EPR forms a dispersed phase. At low ethylene contents, EPR do not influence the morphology of PP. The spherulites crystallise from the melt and separate from the rubber phase, which concentrates in the amorphous phase. At higher ethylene contents EPR reduces the spherulite size [96]. The biggest improvement in such "rubber toughened blends" is an increased impact resistance. The energy dissipates mainly by matrix crazing, which is controlled by the rubber droplets. Blends of PP/EPR and PP/EPDM blends are of huge interest for the automotive industry, which consumes almost 90% of PP-rubber-blends for e.g. fenders, consoles and cloth hooks [51, 52, 79].

2.3.4.3. Homogeneous PP/PP-blends

The molar mass distribution is the main selection criterion of PP for its processing technology, being directly related to the melt viscosity and, therefore to the processability [97]. The melt flow index (MFI) is commonly used as classification for different polymer grades. 33% of PP is used for injection moulding (high MFI), 25% for fibers and filaments, 12% for films (both medium MFI), 7% for extrusion applications (low MFI) and 23% for other applications [1]. The MFI of a theoretical homogeneous secondary recycled PP lies between those of the feedstock components and can be predicted by an additive rule [98]. Thus, the resulting monopolymer blend has normally a broader molar mass distribution compared to a virgin polymer with similar MFI leading to a complex processing problem. According to Hunealt et al. even in a homogeneous PP/PP-blend (with an interfacial tension of zero) a high viscosity ratio leads to the formation of non-homogenised particles [99]. Meller et al. observed melt fracture caused by inhomogeneities in a polyethylene melt with bimodal molar mass distribution [100]. Both authors conclude, that inhomogeneity can be reduced by an optimisation of the mixing parameters during extrusion. However, differences in molar mass and molar mass distribution result in large differences in the mechanical deformation behaviour of PP [101]. In general, toughness of PP increases with craze strength, which is related to the molar mass [102, 103]. So the mechanical properties can be improved by adding a low MFI PP to a high MFI PP. Furthermore, due to the continuously changing composition of post-consumer waste, a pure recycling grade PP-blend cannot reach the high quality standards of a virgin grade PP. Nevertheless compounding of a virgin PP with recycling grade PP can at least add value to the post-consumer material [104]. This topic is well studied in literature and commercially used in primary recycling, but was not introduced to secondary recycling yet.

Another issue concerning PP recycling is that PP post-consumer waste has gone through several processing steps, has been exposed to sun light (UV irradiation) and oxygen and has undergone significant ageing. Therefore, the polymer is partially degraded and undergoes further degradation during reprocessing [105, 106].

2.3.4.4. Degradation of PP

Polyolefins are not biodegradable, but they undergo physical and chemical changes during their life. This process is called ageing. According to DIN 50035 ageing is a collective term of irreversible chemical and physical processes during life time of a polymer [107]. Physical ageing are processes that change the tertiary structure and the morphology of the material like relaxation, post-crystallisation, or processes that generate inhomogeneities of mixed components like phase separation, plasticisers diffusion and agglomeration. In general, physical ageing changes the shape and the structure or physically measurable properties with no chemical causality. Chemical ageing summarises processes that go hand in hand with chemical reactions of the polymer. These reactions primarily affect the molar mass, like post condensation (in case of polyesters), post-polymerisation (thermosets and other resins) and degradation.

Degradation can be thermal, photo-oxidative, thermo-oxidative, hydrolytic, chemical or microbial [107]. Degradation of the most polymers forms smaller oligomers and does not decompose the material to CO_2 and H_2O like biodegradation. In worst case, toxic and environmentally harmful small molecular substances (e.g. BPA from polycarbonate) are formed [11]. In case of the semi-crystalline polypropylene degradation and post-crystallisatio, occur during ageing. Physical ageing affects the amorphous and/or mesomorphic regions of the material and leads to an increase in density and modulus resulting in embrittlement [108]. Degradation is mostly evident by chain scission reaction, affects statistically the high molar mass content of PP mainly and strongly reduces the average chain length. Visual evidence for degradation are discoloration, increase of roughness and loss of gloss. The mechanisms in PP degradation are mostly related to radical reactions. Once the degradation reaction is initiated (reaction scheme in box in Figure 16), oxygen reacts with the radicals forming peroxy-radicals and subsequently, after H-abstraction from other polymer chains, hydroperoxides and new radicals are formed. Hydroperoxides decompose into the corresponding alkyloxy and hydroxyl radical. The latter form alcohol, water and further radicals through H-abstraction from the polymer chain [109].

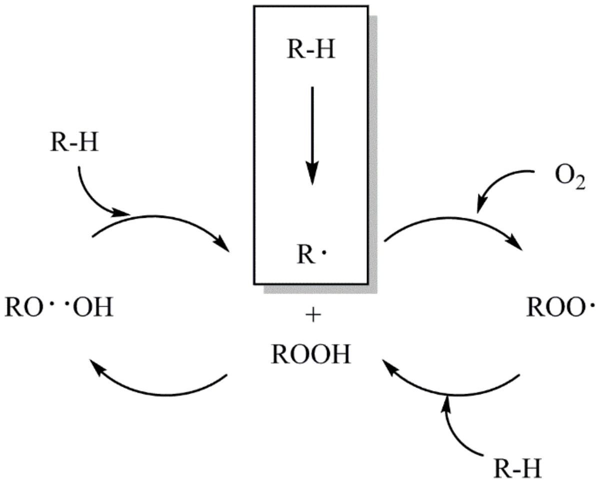

Figure 16: Autooxidation cycle of PP

The initiation reaction of PP degradation is most likely either thermal during processing, or UV-irradiation-induced during its product life [43, 110, 111]. Contrary to PE, PP undergoes only chain scission and no crosslinking, which results in a very fast loss of molar mass during degradation. Fayolle et al. [112] studied the mechanical behaviour of thermo-oxidatively aged PP films with 100 microns thickness. The formation of carbonyl groups to monitor the ageing of the PP was measured by FTIR-spectroscopy. The mechanical performance, by means of elongation at break, deteriorates far before any carbonyl groups in the aged polymer stripes are detected. To prevent radical induced chain scission during product life, PP needs the addition of radical scavengers, called stabilisers [109, 113]. Fayolle et al. [114] also studied the mechanical behaviour of stabilised PP films and found out tha less deterioration caused by degradation, but that chain scission still takes place and reduces molar mass. Contrary to the unstabilised PP in their former study, no carbonyls were formed, but the content of active stabilisers was reduced. Jansson et al. [115] simulated multiple ageing and recycling for PP and observed a “zig-zag”-shaped curve of the elongation at break. The elongation at break dropped after each ageing step and increases again after re-extrusion. They concluded a pronounced crack growth caused by surface degradation and changes in the crystallinity for the drop of the elongation at break. Furthermore, the degraded polymer chains get diluted during re-extrusion, so the material can recover to a certain content. Nonetheless, the material degrades over multiple extrusion steps. Many papers have been published on the topic of thermally induced degradation caused by reprocessing in an extruder during recycling. The simulation of many re-extrusion cycles (Figure 17) showed a significant reduction of elongation at break, an increase of the modulus and a reduction of the toughness of PP. The molar mass was reduced by thermally induced degradation [116, 117, 118, 119, 120, 121].

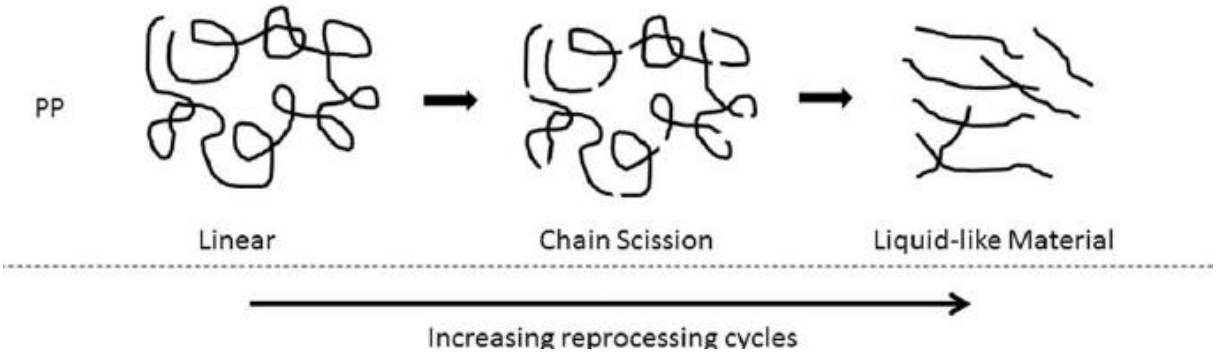

Figure 17: Illustration of PP degradation during reprocessing

Polymers in general, but especially PP, need proper stabilisation during processing and consequently restabilisation for reprocessing [122]. Rust et al. [123] studied the degradation of PP in a possible "closed loop" recycling of PP from car batteries. The use of recycled PP has cost saving implications, but the worsening of the material performance during multiple extrusion is a field of big concern for battery producers. Even with re-stabilisation, the reprocessing of recycled PP reaches its limits.

The high quality standards in industry require adequate restabilisation during every recycling step, otherwise the content of active stabiliser would decrease. On the other hand, with every recycling step the content of non-active species increases. In case of closed-loop recycling – like car battery cases – the stabiliser mixture will not change, but the composition of the stabiliser "cocktail" gets more and more complex, when post-consumer waste is recycled.

2.3.4.5. The stabiliser "cocktail"

Plastics in general offer a broad field of application, but with the choice of the correct additives, the field of application can be significantly expanded. Without any additives, PVC as an amorphous thermoplastic is a stiff polymer (used for pipes and window frames), but when plasticisers (mostly derivatives of phthalic acid) are added, PVC softens and can be used for cable insulations and even blow moulding [109]. However, the legislative pressure has led to a reduction of PVC, PS, and other plastics in packaging, pipes and cable insulation. However, due to the last years of innovation in the field of stabiliser compositions PE and PP have expanded their area of application [124]. Suppliers like BASF offer a big product catalogue of stabilisers, mixtures and master batches thereof and a specific product support for every particular need. The chemical functionalities range from phosphoric acid derivatives for heat stabilisation during production, sulphur containing components for the decomposition of hydroperoxides to hindered phenols for a broad field of thermal radical stabilisation and hindered amines for light stabilisation stabilisers (HALS). The different functional groups interfere at specific points of the autooxidation cycle of PP (Figure 18) and prevent degradation [109].

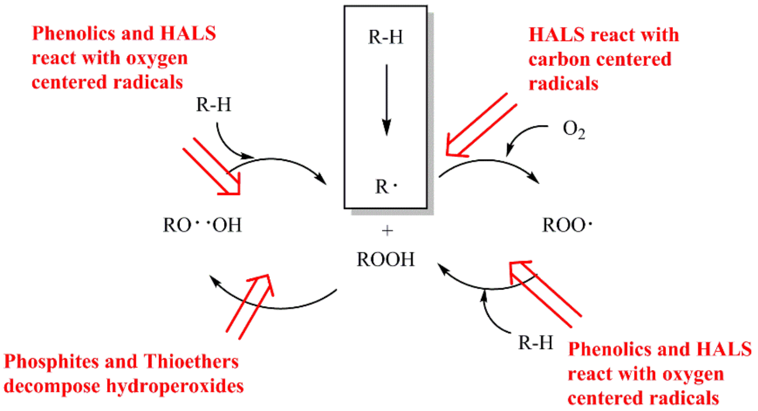

Figure 18: Interruption of the autooxidation of PP by stabilisers

The structure of the chemically active compounds of the stabiliser systems, the substance classes and their field of activity during polymer life and processing are given in Figure 19.

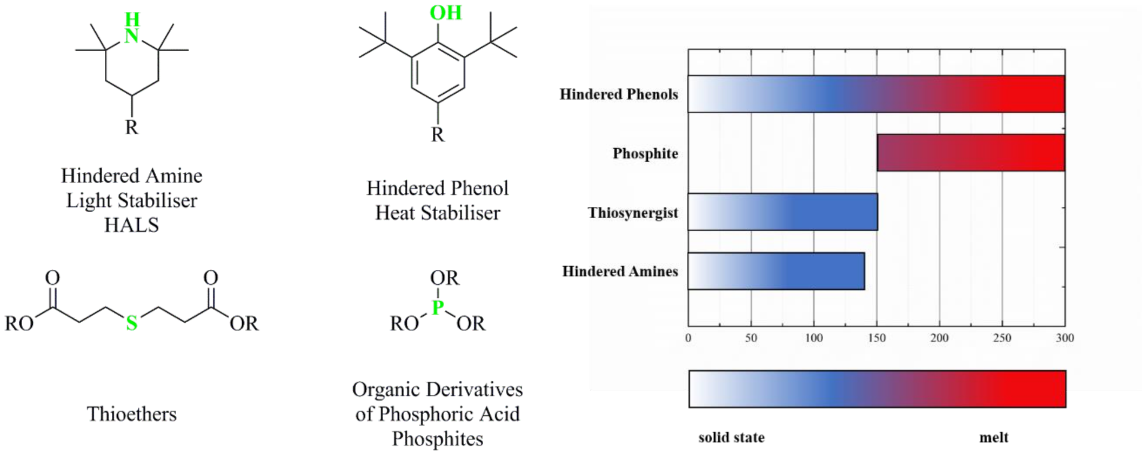

Figure 19: Chemical structure of the active compound (green) of the most common stabilisers and theire field of activity [109]

Stabiliser reactions are of utmost interest, and the co-reactivity of specific stabiliser systems is a challenging topic, with a lot of open questions [113]. Vyprachtický et al. [125] focussed on the interaction between hindered phenol and hindered amine stabilisers and concluded, that the small HALS molecules scavenge radicals very fast and transport the radical to the hindered phenol. The resulting chemical circle is very effective to stabilise the material, but it also fastens the consumption of active stabiliser and depends on the type of ageing (photochemical or thermo-oxidative). Binary stabiliser systems can be studied very well in model mixtures [126], but the unforeseen composition in recycled PP from post-consumer PP is an unpredictable challenge.

Therefore, certain applications of recycled PP, e.g. a water pipe, remain impossible. First, the interactions are not calculable for long-term applications, second some stabilisers could migrate out of the PP matrix and pollute drinking water [127, 128, 129].

In sum, all these points result in higher costs to get a product of high quality from recycled PP – especially from post-consumer waste PP – than from virgin material. All negative factors make other treatments beside landfill and incineration from nowadays state-of-the-art difficult to implement.

2.3.5. Approaches to solve problems in secondary PP recycling

This section will present some approaches for secondary recycling of PP post consumer waste. Primary recycling – as already mentioned – is more a logistically problem, than a technological one. Tertiary and quaternary recycling meet the challenges presented by PP post-consumer waste.

2.3.5.1. Upgrading by restabilisation

Mechanical recycling of thermoplastics for high value applications is directly associated with restabilisation [130]. The partial or total depletion of the stabiliser system in recycled PP is a matter of grave concern, which results in significant degradation during re-extrusion. Thus, restabilisation is mandatory [122]. The auto-oxidation of PP takes place during product life (Figure 16), but at very low reaction rates. As soon as the aged PP is reprocessed, the high temperatures and the molten state cause a dramatical acceleration of degradation [131]. Restabilisation is one the most promising concepts in recycling technology and master batches (e.g. Recyclostab®) are available for this task [132, 133]. Kartalis et al presented a closed loop recycling of post-used garden chairs using Recyclostab®. Based on their results they concluded that restabilisation permits the reuse of the material [59, 134, 135].

2.3.5.2. Addition of heterogeneous fillers

A virgin polypropylene homopolymer has a rather low modulus, a limited impact resistance and high notch sensitivity. To improve the mechanical and thermal properties, additives, such as mineral fillers (calcium carbonate, talcum, carbon black, etc.) [136, 137, 138, 139] or organic fillers [140] are blended with PP [141]. The morphology of these composites is illustrated in Figure 20.

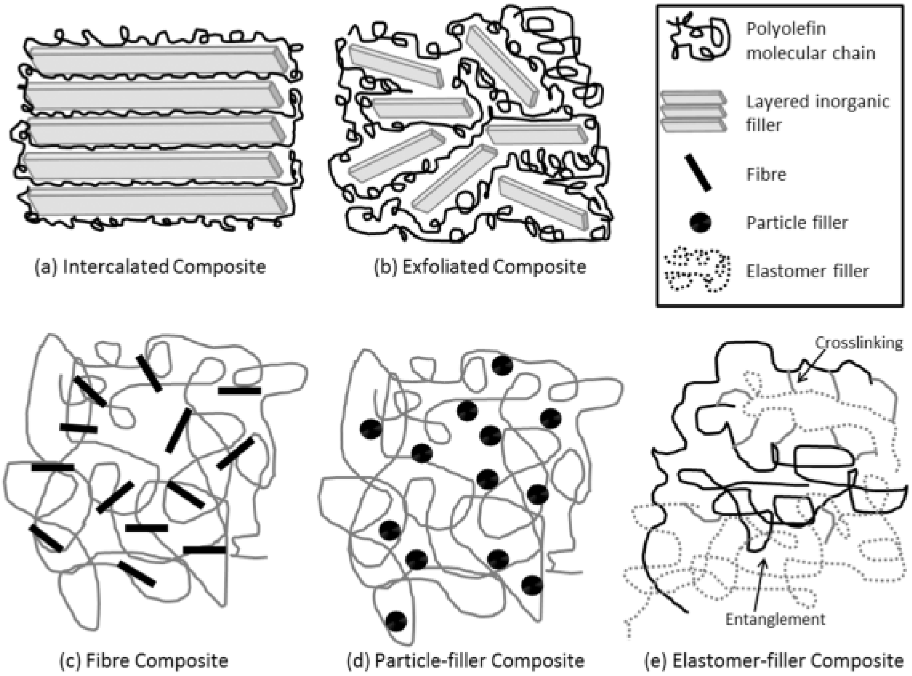

Figure 20: Different types of fillers and their structure [142]

Inorganic fillers like calcium carbonate are often used in combination with elastomers. The inorganic part complements as well as amplifies the effect of the elastomer content. The impact energy is increased, hardness is improved, and modulus and tensile strength is higher, while the costs are lowered [143]. Talcum is used to increase the stiffness, the tensile strength and the creep resistance of PP. The efficiency can be further improved, when surface modified talcum with higher PP compatibility is used [144, 145]. Due to strong interfacial interactions, carbon black has a reinforcing effect in the solid state, as well as in melt, which is shown in a pronounced increase of melt viscosity. Furthermore, the electric conductivity is enhanced, which is favourable for some applications [146]. In recycling carbon black is primarily used for colouring, to conceal the heterogeneous composition of the material caused by the different colour of the recycled flakes [50].

2.3.5.3. Impact modification of PP by blending with PP-rubber

Blending of PP with PP-rubber (saturated ethylene-propylene-diene-copolymer, EPDM or ethylene-propylene random-copolymer, EPR) was already mentioned. Especially the improvement of the impact strength made the addition of ethylene-propylene-copolymers also relevant for the recycling of PP. This has the effect of also reducing the yield strength and Young's modulus and can compensate stiffening derived from degradation. Sometimes, inorganic fillers are added to complement as well as amplify the effect of the elastomer content, when modulus decrease is not favoured [141, 147, 148]. Matei et al. compounded recycling grade PP from injection-moulded containers with different styrene-rubbers and PE-g-MAH. They obtained good properties compared with the unmodified recycling grade PP, suitable for new goods for various applications [149].

Copolymers of propylene and ethylene do not only offer the possibility to improve the mechanical properties of a recycled material, but can also be used to compatibilise immiscible PP/PE-blends [150].

2.3.5.4. Blend compatibilisation

Copolymers became a special field of interest because of their ability to reduce the size of dispersed heterogeneous blend particles especially in PP/PE/EPR-blends [74, 151]. Eagan et al. recently presented a new multi-block-copolymer from ethylene and propylene with supreme compatibilising effects on PP and PE sheets [152]. As already mentioned, the mechanical properties of a heterogeneous polymer blend are influenced by the size of the dispersed phase droplets in the matrix polymer. The size of the dispersed particles depends on interfacial tension, viscosity ratio and mixing efficiency. The interfacial tension is reduced down to nearly zero, if the interface between the PP- and the PE-phase consists of a PP-PE-copolymer [69]. The compatibiliser can fill the interface gap of the immiscible polymers, making the dispersed particles smaller and more uniform and the mechanical performance can be improved, which is illustrated in Figure 21 [153].

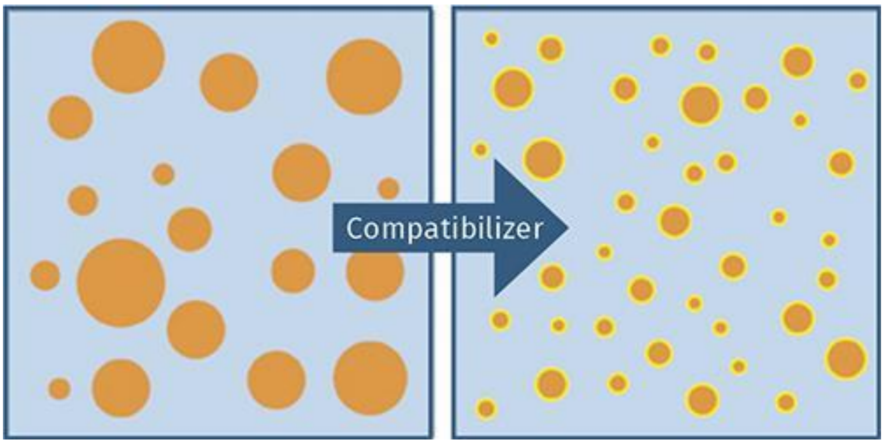

Figure 21: Effect of the addition of a compatibiliser on droplet size

Also compatibilisers for more complex systems like ternary blends are available [154, 155, 156].

In situ compatibilisation – preferably in melt during extrusion – is a more sophisticated variant to improve the mechanical properties of an immiscible blend during its processing. In most cases, a combination of a thermal initiator with an unsaturated monomer is used (e.g. maleic anhydride and benzoyl peroxide) [157, 158]. The initiator activates the polymer chain and a polymerisation from the chain is started. The new graft chain itself can act as compatibiliser (e.g. PP-g-PS for PP/PS-blends), the graft chain can recombine with graft chains from the dispersed phase (e.g. PP-g-MAH in PP/PE-blends), or the graft chain contains of functional groups that can react with the dispersed phase (e.g. PP-g-MAH in PP/EVOH-blends) [150, 159, 160]. In situ compatibilisation offers the possibility to improve the material properties of a commingled plastic feedstock by the addition of chemicals before re-extrusion and restabilisation. Santana et al. for example presented a process to improve the properties of PP/HIPS-blends (high impact polystyrene) from recycled beverage cups [161]. Hettema et al. applied their research on PP/PE compatibilisation on recycled bottle PE-HD containing 10% PP impurities and observed good improvements of the impact strength [162] and also Gu et al. studied reactive blending of recycled polyolefin blends [163].

Concluding, PP offers the possibility of tailor-made solutions for specific needs at a very comfortable cost level. This big advantage of PP over other materials is the major drawback for its recycling. Recycling grade PP will never reach the same standards as *virgin grade PP, not even if there is a high standard of sorting and other technologies like compatibilisation and restabilisation. At least the recycling grade material has to compete with a price of virgin grade below 1 €/kg. The legislative pressure is not expected to increase in the European Union compared to the last years and the price for virgin grade PP is stable since many years and is forecasted to be stable within the next years. Beside the improvement of sorting technologies to generate single polymer waste fractions in recycling facilities, value adding to the recycling grade PP is one of the most important tasks of academic research. Especially for PP a linear recombination, comparable to PET would solve all problems of PP recycling. But for this task, PP lacks of functionalities, offering this possibility. However, chemistry offers also some other approaches.*

2.4. Long chain branching of PP

Linear polymers are known for their low melt strength. Standard linear iPP homopolymer consists of linear chains with a relatively narrow molar mass distribution and shows poor processing characteristics in processes where extensional flows dominate. For PP to be used in fields of applications where the melt strength plays an important role e.g. at high shear rates and at virtually zero shear rates, modifications are needed to enhance the strain hardening behaviour of its melt in such flows. The extensional viscosity of an unbranched polymer melt usually matches the threefold (Trouton ratio) of the shear viscosity curve. A strain hardening melt shows a stiffening on drawing, which can be described by a deviation from the linear viscoelastic behaviour in extensional flow [164]. In processes like foaming, thermoforming, blow moulding and film blowing, strain hardening and high melt strength are desirable properties of the polymer melt. The melt strength of a polymer is a measure of the tenacity of the melt and is defined as the maximum force by which a molten thread can be drawn under standard conditions before it breaks. Increasing the melt strength to get high-melt-strength-PP (HMS-PP) refers to a melt becoming stiffer and stronger by the formation of a higher number of chain entanglements. According to the theory of polymer entanglement, there are three possibilities to increase the number of entanglements: Increase of molar mass, broadening of molar mass distribution and branching [165]. Such branches require a molar mass of the side chain higher than the entanglement molar mass (M_e) of the polymer to form a successful chain entanglement. If this requirement is fulfilled, the side chain is called long chain branch (LCB; Figure 22). Even though a very broad (e.g. bimodal) molar mass distribution can improve this behaviour, strain hardening is most efficiently achieved by LCB. It is expected that if the melt strength behaviour of PP is improved, its market position will become even more prominent, replacing other thermoplastics in several applications [43, 166].

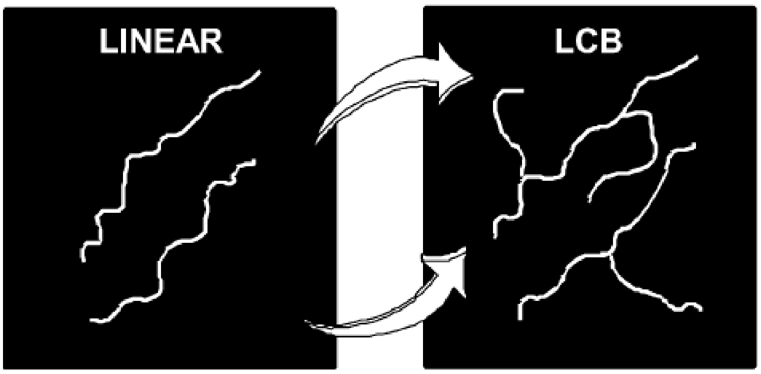

Figure 22: Long chain branching of PP [167]

In case of PP, LCB is an industrial post-reactor process, where a linear virgin PP is used as precursor. Several commercial grades of HMS-PP are available:

Himont (later LyondellBasell) was the first who introduced HMS-PP to the market in 1990 [168]. The HMS-PP was produced by electron beam irradiation in solid state. Thereby the radicals are generated far below the melting temperature and beta-scission of the PP is inhibited. The branching reaction takes place in the amorphous phase of the polymer by recombination of PP chains [169, 170]. LyondellBasell ceased the HMS-PP production in 2008.

Since 2010, Borealis offers HMS-PP under the tradename Daploy™, which is produced by a reactive extrusion process, for blow moulding and foaming. According to their patent, the reactor grade PP-powder is loaded with 2% 1,3-butadiene and an organic peroxide with high activation temperature. 1,3-Butadiene acts as linking and stabilising agent for the branching process and reduces beta-scission during the reactive extrusion [171].

Other companies extended their portfolio and started to produce HMS-PP later. For example Braskem from Brazil and the Total in France entered the market in 2016 with their products [172, 173], Chevron Philipps Chemical Company also holds patents in this field [174].

Due to the chemical nature of PP, radicals must be used to initiate the chemical modification. The attack of a radical on PP leads to an abstraction of a hydrogen at the tertiary carbon. The tertiary carbon radical is unstable and undergoes β-scission (Figure 11). It is well known that β-scission strongly depends on temperature. Below 60°C the recombination rate overwhelms the rate of β-scission and becomes predominant and as a consequence cross-linking occurs. Above 60°C, the situation changes and β-scission increases, which decreases the molar mass of the PP exponentially by degradation. The resulting negative effects of degradation (reduced viscosity, embrittlement, increasing modulus, decreasing impact resistance,..) are a limitation of chemical modification of PP [46].

In general, PP can be modified in solid state and in melt. Reactions on PP in solid state are well summarised by Rätzsch et al. [167], especially with focus on LCB of PP [175]. Electron- and gamma beam irradiation or peroxide initiation are possible methods to generate radicals for LCB in solid state (Figure 23).

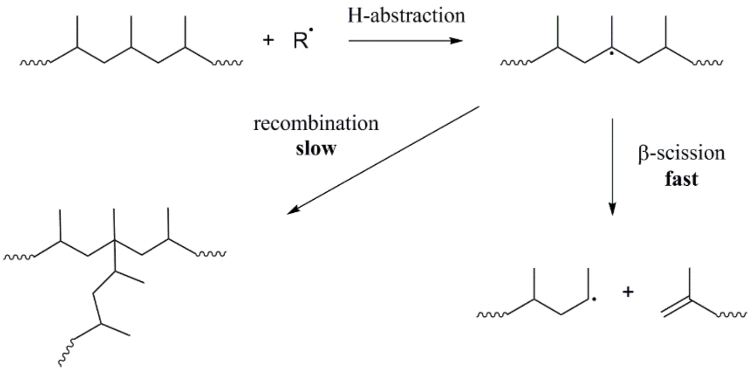

Figure 23: LCB of PP in solid state without additives

The LCB efficiency increases when unsaturated organic compounds are added [167, 176, 177]. The solid phase structure influences the diffusion of the monomers to the reaction sites in the amorphous phase of the polymer. In addition, the compatibility of the monomer with PP is of big importance and determines how much monomer can be loaded on the particles. For example reactor grade PP powder can absorb 0.25% of styrene within one minute and only 0.005% 1,3-Butadiene in solid state at room temperature [178].

Modification in melt enables the transformation from linear to LCB-PP and pelletizing in one processing step. LCB in melt needs to focus on partial stabilisation of the tertiary radical to control β-scission. Wong et al. used for example styrene as resonance stabilising monomer. Styrene shows good compatibility with PP and is well soluble in the PP-melt. The monomer has a high affinity to the PP-macroradical and generates a resonance stabilised intermediate state [179]. Daploy™ process uses the same concept and uses 1,3-butadiene as resonance stabilising monomer for LCB [167]. Figure 24 shows the reaction scheme of LCB in melt under assistance of a monomer described by Rätzsch. The monomer M stabilises the macroradical before and after chain scission and builds a bridge between the molecules at the cross-link. Other monomers for LCB of PP in melt are divinyl benzene [180], vinylsiloxanes and vinylsilanes [181, 182], pentaerythritol tri- and tetraacrylate [183], pentaerythritol tetraallylether [184], trimethylol propane triacrylate [185], triallyl cyanurat [186], 1,4-butanediol diacrylate and 1,6-hexande dioldiacrylate [187, 188].

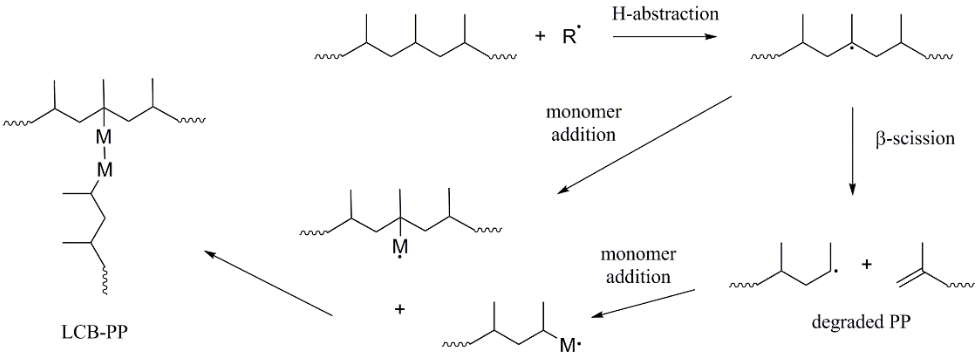

Figure 24: LCB in melt with resonance stabilising monomer

LCB in two steps was presented by Cao et al. with maleic anhydride grafted PP and a difunctional amine. Branches are generated by the reaction of the anhydride with the amine by forming an imine [189].

During the last years, many research articles have been published showing further improvements of the LCB-efficiency with polyfunctional monomers by using co-agents. Hydrochinone not only reduces the amount of crosslinked particles during in situ compatibilisation of PP/PE-blends, it also reduces cross-links in PP grafting with polyfunctional monomers [190]. Further improvements to control the architecture of the PP structure during its functionalisation were reviewed by Passaglia et al. [191] and Drooghaag et al. [192]. The most promising chemical compounds are derivatives from heteroaromatic ring compounds like thiophenes and furans [193], dithiocarbamates [194] and nitroxides like tetramethyl-piperidinoxyl (TEMPO) [195]. Heteroaromatic ring compounds undergo a chemical bond with the PP macroradical and form a resonance stabilised complex that acts like a bridging molecule by reaction with a second PP macroradical. This is shown in Figure 25 according to Coiai et al. [196].

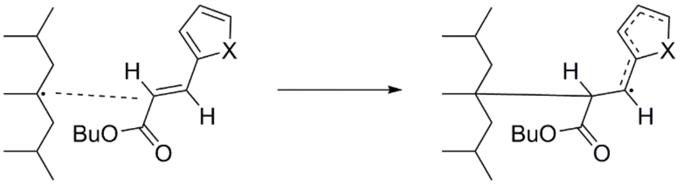

Figure 25: Heteroaromatic ring compounds and the corresponding resonance stabilsed macro-radicals. X=O, S

Other sulphur containing co-agents as dithiocarbamates are also known as chain transfer agents and are used in organic chemistry to synthesise polymers with tailor made properties. The general structure and the mechanism of macroradical stabilisation of such a dithiocarbamate based co-agent is shown in Figure 26. The co-agent undergoes a reversible bond with the macroradical and prevents the PP from chain scission and prolongs the life time of the macroradical [197].

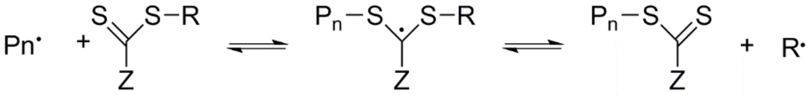

Figure 26 Reversible addition fragmentation chain transfer between a dithiocarbamat and a polymer [198]

According to Lagendijk et al. peroxydicarbonates (PODIC) combine partial stabilisation of the PP-chain and the initiation of the LCB-reaction. Especially peroxydicarbonates with long aliphatic chains were described as very efficient with respect to LCB per 1000 carbon atoms [199]. A detailed study on the PODIC mediated LCB reaction in melt has not been provided yet, according to the developers the formation of an alkylcarbonate-polymer adduct is suggested to stabilise the macroradical [200]. A general reaction scheme is given in Figure 27.

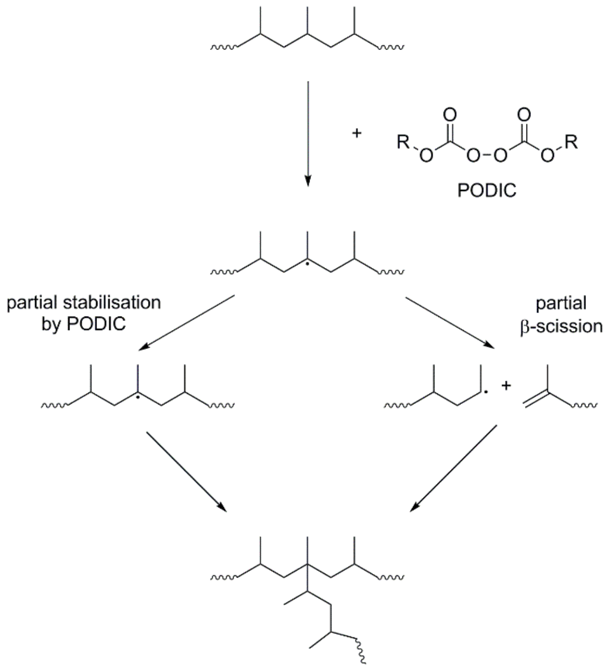

Figure 27: PODIC assisted LCB of PP

Because of their length, long chain branches act locally as individual molecules, are flexible and produce entanglements. The hydrodynamic volume of the branched chain is smaller than a linear chain with the same molar mass (provided that the polymer coils act like ideal chains in “theta condition”) [164]. This substantial impact allows the detection of LCB by size exclusion chromatography. It is possible to quantify LCB by comparing the solution properties of a branched polymer and a linear equivalent using the Mark-Houwink plot to calculate the radius of gyration according to the model of Zimm and Stockmeyer. However, the relation between the radius of gyration and the hydrodynamic volume is complex in the case of branched polymers [201]. The molecular architecture of LCB polyolefins influences not only the viscosity of the polymer in solution, but also the melt viscosity. The introduction of LCB induces a higher level of melt elasticity, increases the zero shear rate viscosity η^0, reduces viscosity at higher shear rates, rises the relaxation time and the values of elastic modulus, and a strong enhancement of the melt strength of the molten polymer [166]. Another method for the detection of LCB is nuclear magnetic resonance (NMR) technique. Shroff and Mavridis showed that NMR-spectroscopy can help to detect LCB between 0.3-3 branches per 10 000 molecules. NMR-spectroscopy is a direct method, but in a polymer that contains short and long chain branches the NMR-technique lacks in its ability to differ between these two types. Also Shroff and Mavredis conclude that rheology is the preferred method for the characterisation of LCB due to the dramatic sensitivity of the zero shear viscosity on the number of long chain branches [202].

2.5. Rheological characterisation of LCB-PP

Molten polymers are viscoelastic amorphous materials, which can be described by the viscosity η. The melt viscosity is most commonly measured by shear tests between two plates. Shear viscosity is calculated from the quotient of shear stress and shear rate. Polymer melts are non-Newtonian fluids, their η shows a dependency on the shear rate and reaches a Newtonian plateau at very low shear rates (zero shear viscosity η_0). The rheological properties of a polymer depend on its weight average molar mass M_w, molar mass distribution (described by the quotient of average weight molar mass and number average molar mass M_w/M_n) and the molecular structure. Molecules with higher M_w show effects like shape memory, because of the higher number of entanglements, and therefore higher relaxation times. M_w determines the absolute value of η_0 and is linked by equation 4 [203]:

$$\eta_0 = K * M_w^{\alpha} \tag{4}$$

Polymers with M_w smaller than the critical entanglement molar mass M_c are in direct correlation with η_0 ($\alpha = 1$ if $M_w < M_c$). M_c is equal twice of the molar mass of two successive entanglements ($M_C \approx 2M_e$). M_e is specific for each polymer, for PP M_e = 5.1-6.9 kg/mol [204, 205] For polymers with higher M_w α is approximately 3.4-3.6 [165], for polypropylene α was found to be 3.5 [206]. The factor K is influenced by the chain stiffness of the molten polymer, which depends in case of PP on the tacticity and temperature.

M_w/M_n influences the shape of the viscosity curve. According to Fleissner et al. M_w/M_n between 3.2 and 10.7 have no influence on the correlation of M_w and η_0 [207]. However, the polydispersity of a polymer melt correlates very well with the crossover point of the modulus curves, which is depicted in Figure 28 [208].

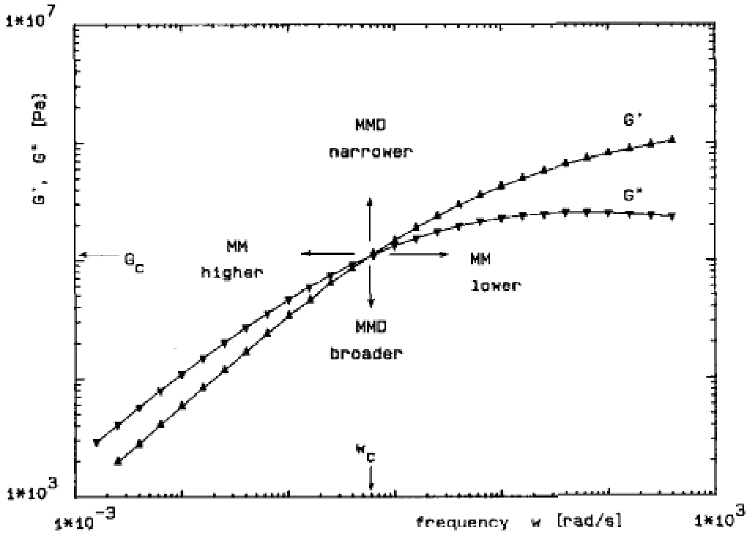

Figure 28: Dependence of G' and G'' on the M_w *and the MMD on the cross over point [207]*

Linear polymers with broader molar mass distributions (MMD) have a larger transition from non-Newtonian to zero-shear plateau. The rheological properties of a polymer melt can be predicted from the molecular parameters and vice versa. In case of LCB polymers, the correlation between molecular structure and viscosity becomes more complex. The exact distribution of LCB per molecule cannot be determined. However, the position, the length and the distribution of branches of a molecule significantly influence η of polymers.

For star like polymer melts with one LCB per molecule, Ball et al. showed an exponential dependency of the ratio of the molar mass of the side arm and M_e on molar mass dependency of the zero shear viscosity [209]. Mc Leish et al. and Daniels et al. reported similar observations also for comb like branched molecules [210, 211]. Janzen et al. studied PE-HD with very small amounts of LCB and described an increase of η_0 with small amounts of LCB and a decrease with higher amounts of LCB [212]. This correlation was also shown by Gabriel et al. with PE [213] and by Tsenoglou et al. for PP [214]. Compared to a linear PP, LCB-PP with similar molar mass has higher zero shear viscosity and pronounced shear thinning at higher shear rates, which is shown in Figure 29.

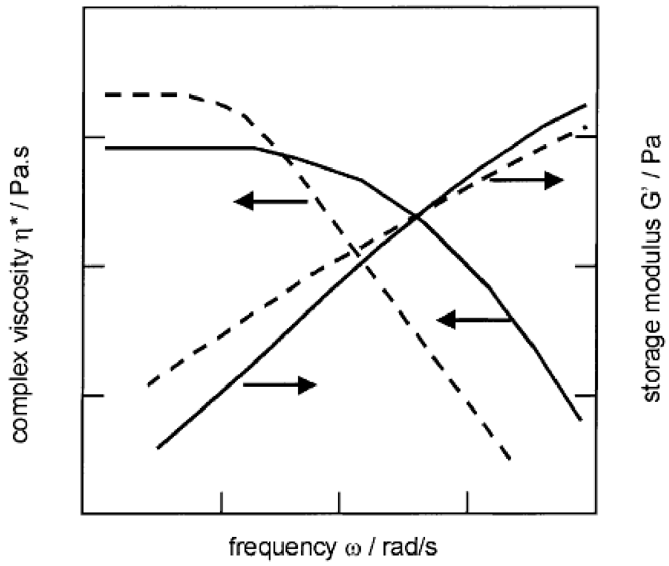

Figure 29: Comparison of the shear viscosity curves of a linear PP (solid line) and a LCB-PP (dashed line) [206]

The main difference of LCB-polymers from their linear types are the deviation from the linear viscoelastic "Trouton" behaviour in extensional flow. The rheological properties in extensional flow are very important for many manufacturing processes of plastics. Time dependent shear rheology and extensional rheology are related to each other by a factor of three (Trouton ratio). A nonlinear deviation from linear viscoelastic behaviour is called strain hardening. Figure 30 shows the time dependent extensional viscosity of a linear PE and a slightly LCB-PE with similar molar masses and illustrates this strain hardening.

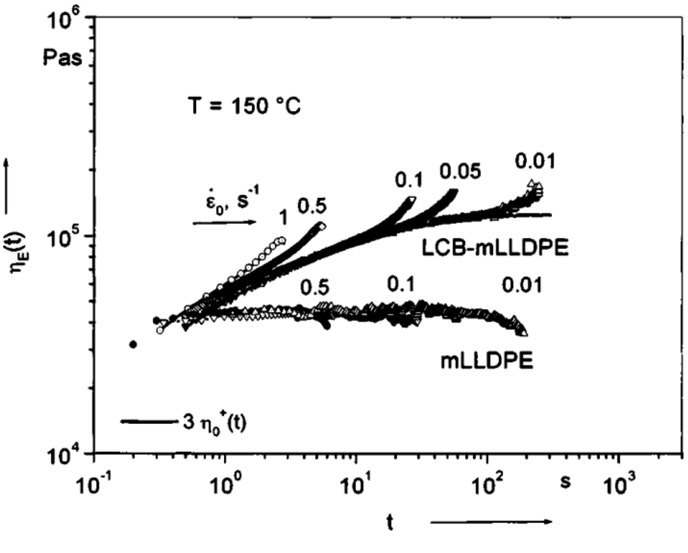

Figure 30: Comparison of time dependent extensional viscosity of a linear LLDPE and a LCB-LLDPE [215]

Strain hardening is a desirable melt property and leads to self-healing effects, which becomes important during foaming and film blowing. Meissner described the first rheometer to measure the properties of a polymer melt in extensional flow [216]. This rheometer was improved by Münstedt [217]. Their device can be described as tensile test machine, the clamps and the sample are in a thermostat filled with silicone oil with similar density like the polymer melt. Thereby sagging is supressed and very low strain rates can be obtained. First measurements are reported with polystyrene and PE-LD samples. The Münstedt rheometer also offers the possibility to study the morphology of the stretched polymer sample [218]. Another extensional rheometer test fixture was constructed by Sentmanat et al. for conventional torsional rheometers [219]. However, the SER-tool (Sentmanat extensional rheometer, Figure 31) is limited to polymer melts with higher zero shear viscosity.

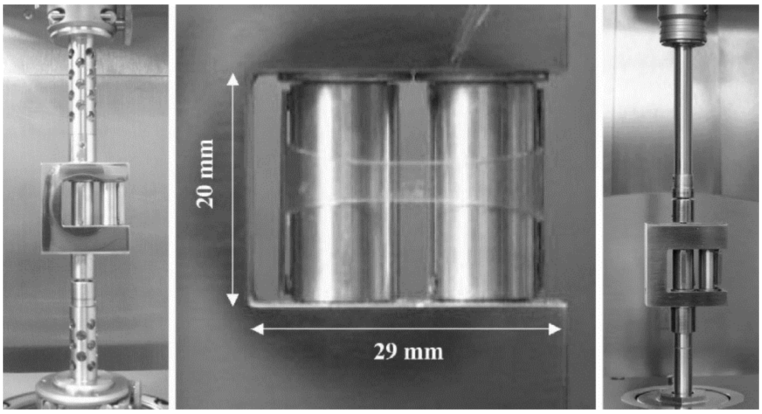

Figure 31: Sentmanat extensionl fixture for torsional rheometer [219]

Strain hardening occurs in polymer melts with broad or bimodal molar mass distribution. Sugimoto et al. studied an immiscible system of HMS-PP with small amounts of high molecular weight PE. Beyond a certain critical strain, the uniaxial extensional viscosity showed rapid increase, which was referred to as strain hardening [220, 221].

According to Wagner et al. strain hardening of linear polymer melts can be accounted for by a tube diameter that decreases affinely with the average stretch. Long-chain-branched polymer melts show enhanced strain hardening in extensional flows due to the presence of long-chain branches. The presence of LCB leads to more chain stretching. This can be quantified by a molecular stress function. The ultimate magnitude of the strain-hardening effect is considered specific for the polymer melt and depends on the molecular weight distribution and branching topology [222]. Consequently, Gabriel et al. observed four different types of strain hardening for PE of various branching structures. From their experimental results, they concluded a strain rate dependency of the strain hardening and different strain hardening ratios in dependence on the molecular structure [215]. Gabriel’s observations where proven by Wang et al. who synthesised LCB-PP (polypropylene-g-poly(ethylene-co-1-butene) by ionic grafting of PP with defined amounts of p-(3-butenyl)toluene with very well defined molecular structure. Thereby they were able to study several lengths of the graft chains, as well as different number of LCB per molecule [223, 224]. Similar observations are also reported by Kempf et al., who synthesised PS with well-defined comb architecture and controlled degree of LCB [225].

Elongational viscosity provides a method to measure the stress-strain behaviour of a polymer in melt and helps to describe the behaviour of a polymer where extensional flows occur. Extensional flows occur during extrusion of a polymer melt, but the most important applications are processes where the melt is suddenly extended like in film blowing and in foaming. Factors of weight savings, recyclability processability and a wider spectrum of properties are driving the fast-growing market of foams. Thanks to its unique melt strength, HMS-PP prepared by LCB post-reactor reaction, can compete with other polymers used in this field.

2.6. Foaming of PP

Polymer foams represent only a small field in global plastic market. Commonly they are used for insulation, packaging and sports. Among thermoplastic foams, foams from PP have several advantages over other plastics, because of its favourable material properties like the chemical resistance, the high melting temperature and the high strength. The basic principle of foaming is mixing of the polymer with a foaming agent, varying of one physical parameter (temperature or pressure) to initiate cell nucleation and expanding (illustrated in Figure 32). In physical foaming the polymer is directly mixed with a gas, chemical foaming requires special agents that release a gas after a chemical reaction (mostly decomposition). Modern foaming agents are expandable microspheres, which consist of a gas filled porous material, and generate the cell by compression and expansion [226].

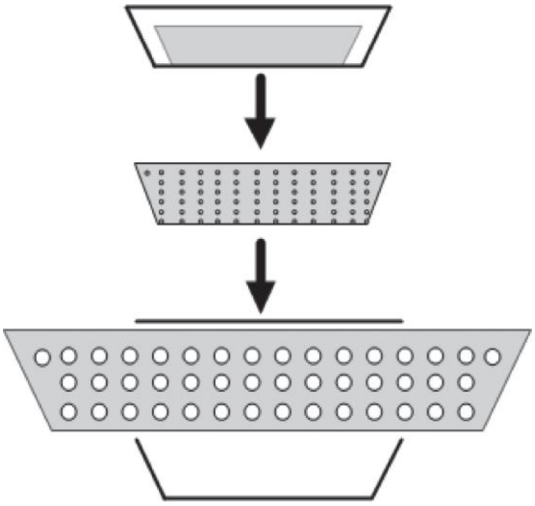

Figure 32: Illustration of the formation of a foamed structure [227]

Compared to PS (standard resin for foaming), unmodified linear iPP has a very low melt strength, which results in cell coalescence (partial or total opening of the cell wall of two neighboured cells) and is therefore not suitable for foaming [227]. In the case of linear PP, higher melt strength and a larger expansion ratio correlate with rising molar mass, which is shown in Figure 33. The cell walls of a material with higher melt strength are able to withstand larger gas pressures before they break.

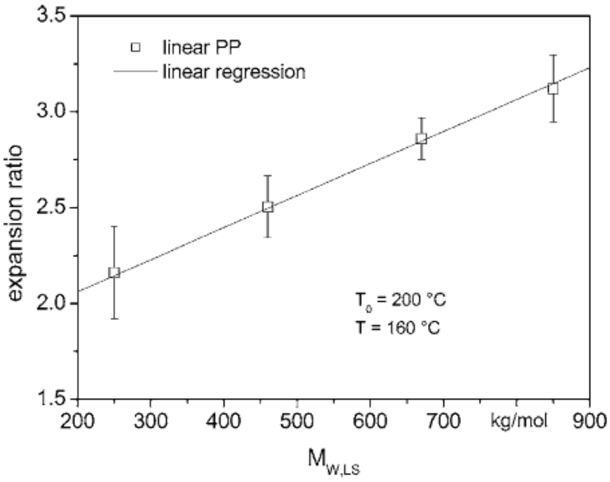

Figure 33: Expansion ratio of several PPs with $scCO_2$ as foaming agent. The PP was loaded with $scCO_2$ at 200°C and expanded at 160°C [228].

Besides the melt strength, the strain hardening behaviour of the material plays a dominant role in foaming. It leads to an increase of the melt strength compared to an equivalent material without strain hardening. To explain this observation, Stange et al. concluded that the more uniform deformation associated with strain hardening is decisive for foaming, too. A more uniform stretching of the polymer melt in the cell walls shifts their rupture to higher expansion ratios. This is more pronounced for polymers that strain harden at higher strain rates [228]. As it is widely known from laboratory experiments how the molecular structure of a material influences elongational flow, this knowledge could be used to support the optimization of the foaming of PP from post-consumer waste.

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3. Materials and methods

3.1. Materials

All used polymers are produced by Borealis. The information given in columns “data sheet” in the tables below was taken from the material data sheets provided on the homepage of the company. The data in the column “TU Wien” have been determined according to the methods presented in the next chapter. The molar mass determination was conducted at JKU Linz. The materials have been chosen to represent the big variety of PP and different products that are part of PP post-consumer waste. To increase the efficiency of the chemicals, the granules and the post-consumer waste was shredded in a Fritsch granulator “Pulverisette 16”. The produced flakes had a mean diameter of 1 mm.

PP HA104E (PP1) is a natural high molar mass and low melt flow rate polypropylene homopolymer, characterised by well-balanced stiffness to impact strength at increased processing properties. The material is recommended for non-pressure pipes and fittings, structured wall pipes and profiles. The physical properties are given in Table 1*Table 1*.

Table 1: Physical properties of PP HA104E (PP1)

Method		**Data sheet**	**TU Wien**
MFR (DIN 1133; 230°C; 2.16 kg)		0.75 g/10min	---
Zero shear viscosity η^0		---	60 800 Pa·s
T_m (DSC)		163°C	163°C
Molar mass		High	M_w = 559 kg/mol M_n = 321 kg/mol
Impact Strength (notched)	Charpy DIN 179	4.5 $\mathrm{kJ/m^2}$	---
	Tensile DIN 8256	---	43.6 ± 4.7 $\mathrm{kJ/m^2}$

PP HC600TF (PP2) is a PP homopolymer with very good melt stability, good processability, stiffness and impact balance intended for thermoformed packaging applications. The product is also suitable for the production of monofilaments, tapes, slits and split films. Typical applications are in line and off line thermoforming, housewares and thin wall packaging, margarine tubes and dairy containers, blends with copolymers, stretch tapes and woven fabrics. The physical properties are given in Table 2.

Table 2: Physical properties of PP HC600TF (PP2)

Method		**Data sheet**	**TU Wien**
MFR (DIN 1133; 230°C; 2.16 kg)		2.8 g/10min	---
Zero shear viscosity η^0		---	18 800 Pa·s
T_m (DSC)		164°C	163°C
Molar mass		Medium	M_w = 394 kg/mol M_n = 198 kg/mol
Impact Strength (notched)	Charpy DIN 179	4 kJ/m²	---
	Tensile DIN 8256	---	39.6 ± 5.9 kJ/m²

PP HD601CF (PP3) is a homopolymer film resin suitable for the manufacturing of unoriented film on chill roll process. The product is optimised to deliver easy processability, high stiffness, good mechanical properties, heat sterilisable and good optical properties. It is recommended for textile, flower and food packaging films. The physical properties are given in Table 3

Table 3: Physical properties of PP HD601CF (PP3)

Method		Data sheet	TU Wien
MFR (DIN 1133; 230°C; 2.16 kg)		8.0 g/10min	---
Zero shear viscosity η^0		---	6 100 Pa·s
T_m (DSC)		162°C	161°C
Molar mass		Medium	M_w = 300 kg/mol M_n = 151 kg/mol
Impact Strength (notched)	Charpy DIN 179	3.0 kJ/m²	---
	Tensile DIN 8256	---	23.9 ± 3.9 kJ/m²

PP HF700SA (PP4) is a PP homopolymer intended for injection moulding and has excellent balanced mechanical properties and is easy to process. The material has been developed for household applications. The physical properties are given in Table 4.

Table 4: Physical properties of PP HF700SA (PP4)

Method		Data sheet	TU Wien
MFR (DIN 1133; 230°C; 2.16 kg)		21 g/10min	---
Zero shear viscosity η^0		---	2 200 Pa·s
T_m (DSC)		164°C	163°C
Molar mass		Low	M_w = 227 kg/mol M_n = 99 kg/mol
Impact Strength (notched)	Charpy DIN 179	2.0 kJ/m²	---
	Tensile DIN 8256	---	19.9 ± 6.4 kJ/m²

PE CG9620 (PE1) is a high-density PE film grade which combines excellent extrusion behavior with superior mechanical properties. The material is recommended for coated films and co-extrusion applications. It is optimised for high temperature resistance, high grease resistance, improved water vapour barrier and excellent processability. The physical properties are given in table 5.

Table 5: Physical properties of PE CG9620 (PE1)

Method		**Data sheet**	**TU Wien**
MFR (DIN 1133; 230°C; 2.16 kg)		12 g/10min	---
Zero shear viscosity η^0		---	983 Pa·s
T_m (DSC)		131°C	132°C
Molar mass		---	M_w = --- M_n = ---
Impact Strength (notched)	Charpy DIN 179	---	---
	Tensile DIN 8256	---	---

Mixed post-consumer waste PP/PE-blend (rBlend)

PP was collected from household post-consumer waste containing yoghurt, vegetable and beverage cups (thermoformed PP), boxes for rigid packaging (injection-moulded PP), bottle caps (injection-moulded PE-HD), and chewing gum containers and milk bottles (extrusion blow-moulded PE-HD). The material feedstock contained of 30% thermoformed PP, 60% injection moulded PP and 5% injection moulded PE-HD and 5% extrusion blow moulded PE-HD. The resulting blend had a grey-blue colour, the physical properties are given in Table 6.

Table 6: Physical properties of mixed post-consumer PP waste (rBlend)

Method	**TU Wien**	
MFR (DIN 1133; 230°C; 2.16 kg)	21 g/10min	
Zero shear viscosity η^0	1 187 Pa·s	
T_m (DSC)	164°C	
Molar mass	---	
Impact Tensile Strength (notched) DIN 8256	14.8 ± 1.9 kJ/m^2	

Single polymer post-consumer waste PP (rPP)

A single polymer waste fraction was sorted manually from thermoformed beverage, food and yoghurt cups. The cups were transparent or white, the resulting mixture hat a grey to white colour, the physical properties are given in Table 7.

Table 7: Physical properties of single polymer post-consumer waste PP (rPP)

Method	**TU Wien**	
MFR (DIN 1133; 230°C; 2.16 kg)	7.5 g/10min	
Zero shear viscosity η^0	8 546 Pa·s	
T_m (DSC)	164°C	
Molar mass	---	
Impact Tensile Strength (notched) DIN 8256	37.1 ± 3.5 kJ/m^2	

PP WE100HMS Daploy™ is a structurally isomeric modified PP homopolymer. The material is intended to be used as modifier in PP coating grades to improve processing and reduce neck. The physical properties according to the product data sheet are given in Table 8.

Table 8: Physical properties of PP WB100HMS

Method	**Data sheet**
MFR (DIN 1133; 230°C; 2.16 kg)	10 g/10min
Zero shear viscosity η^0	---
T_m (DSC)	162°C
Molar mass	M_w = 340 kg/mol M_n = 85 kg/mol

PP WB140HMS Daploy™ is a structurally isomeric modified PP homopolymer with long chain branches. The material has been developed for foaming applications in automotive and food packaging, or foamed sheet converting technologies. The physical properties are given in Table 9*Table 9*.

Table 9: Physical properties of PP WB140HMS

Method	**Data sheet**
MFR (DIN 1133; 230°C; 2.16 kg)	2.1 g/10min
Zero shear viscosity η^0	---
T_m (DSC)	159°C
Molar mass	M_w = 360 kg/mol M_n = 60 kg/mol

3.2. Methods

3.2.1. Methods for LCB

3.2.1.1. *LCB with styrene and peroxide*

According to Wong et al. a combination of styrene and 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (organix peroxide with high decomposition temperature) (Figure 34) is suitable for rheological modification of PP [1]. Styrene (≥ 99%, Aldrich) and Peroxan HX were used without any purification. Peroxan has a half life time of 10 h at 115°C and releases three radicals after decomposition [2].

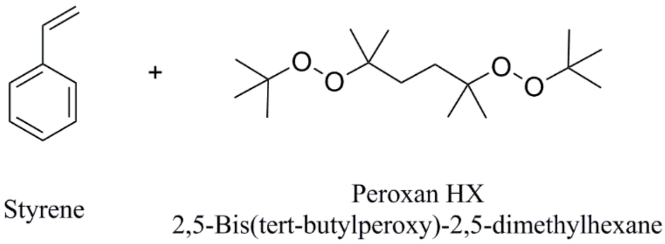


Figure 34: Structure of the used chemicals

The recombination depends on the degree of grafting and turns from chain scission (the ratio of monomer and peroxide is low) to recombination and LCB and finally to crosslinking (the ratio of monomer and peroxide is high). A reaction scheme is given in Figure 35.

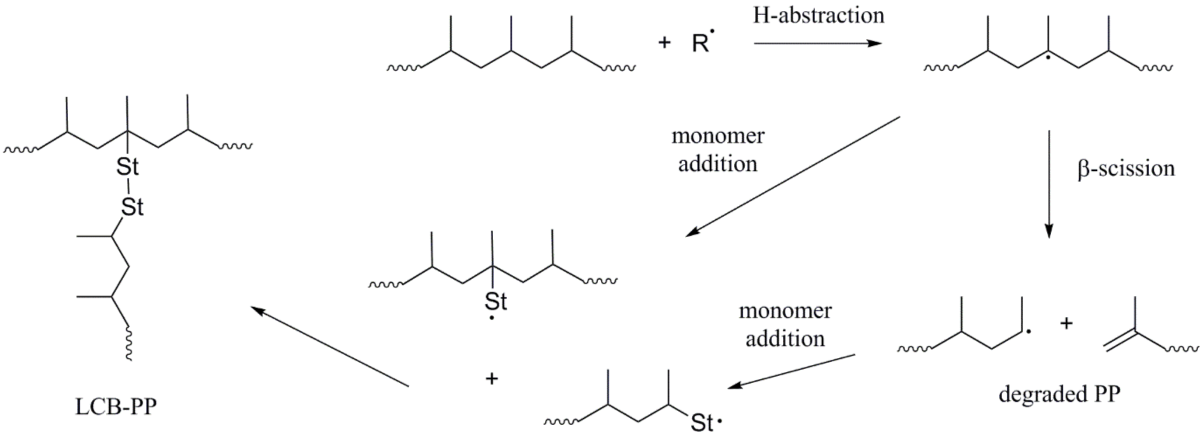


Figure 35: Reaction scheme of LCB with styrene and a peroxide according to Wong et al. [1]

Preliminary experiments have shown that the optimum window of opportunity for LCB with styrene and peroxide is a molar ratio of radical and monomer of 1:8 (see chapter

4.1.2., p. 77). Two concentrations have been chosen that fulfil this requirement. The Abbreviation and the exact specifications are given in Table 10*Table 10*.

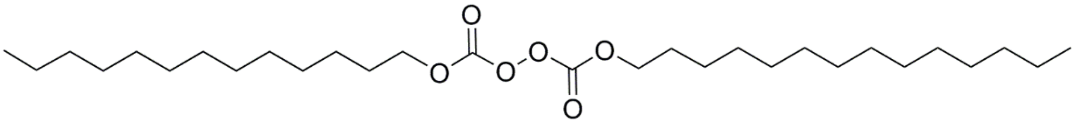
Table 10 Specifications of the optimum parameters of LCB with styrene and peroxide

Abbreviation	Sample specification
-A1	20 mmol/kg peroxide (5.8 g/kg), 480 mmol/kg styrene (50 g/kg)
-A2	35 mmol/kg peroxide (10.2 g/kg), 840 mmol/kg styrene (87.5 g/kg)

Styrene and peroxide were premixed and the liquid was dropped on the polymer flakes and was stored overnight to allow the chemicals to diffuse into the particles.

3.2.1.2. LCB with Dimyristylperoxydicarbonat

According to Lagendijk et al. peroxydicarbonates (PODIC) with long aliphatic side chains have good LCB efficiency during reactive extrusion [3]. One commercially available PODIC is Dimyristylperoxydicarbonate, which is used in industry as initiator for polymerisation reactions (trade name e.g. Peroxan C126). The chemical structure is given in Figure 36.



Peroxan C126
Dimyristylperoxydicarbonat

Figure 36: Chemical Structure of Peroxan C126

Buback et al. [5] studied the decomposition of di-myristyl-peroxydicarbonate (Figure 37). Two alkoxy carbonyloxyl radicals are formed by homolytic cleavage of the O-O-bond of species (I) forming (II). If the time interval is sufficiently large, (II) decarboxylates by eliminating carbon dioxide, producing two alkoxy radicals (III) [4]. Species (III) is expected to abstract hydrogen from PP generating the PP-macroradical. The improvement in melt strength is assumed by stabilisation of the PP-macroradical due to the recombination with (II) and the formation of an alkylcarbonate-polymer adduct.

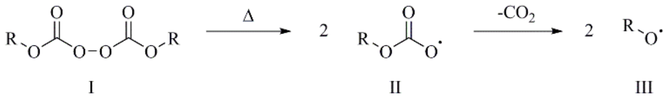


Figure 37: Decomposition of PODIC

The white powder was dissolved in n-hexane and was dropped on the polymer flakes for a homogeneous distribution on the polymer. According to Gotsis et al. a concentration of 20 mmol/kg PODIC (10.3 g/kg) has been chosen for the melt modification [6]. This concentration has shown the best results, with respect to foamability.

3.2.2. Reactive extrusion

3.2.2.1. Laboratory Scale

Reactive extrusion was carried out in a Haake Mini Lab II conically shaped twin-screw extruder (Figure 38) at 180°C and 100 rpm screw speed for 6 min. After 5 min, when the peroxides should be completely decomposed (estimated from half life time), 1 mg (about 0.02%) Irganox 1010 (pentaerythritol tetrakis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate) was added in order to prevent further degradation.

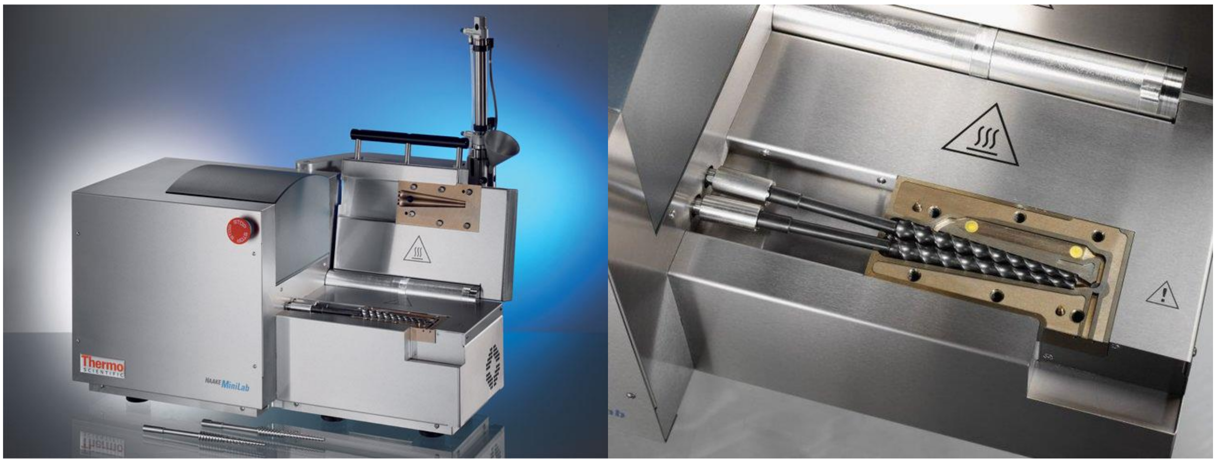


Figure 38: Haake Mini Lab 2 laboratory extruder [Source Haake]

3.2.2.2. Scale Up

Experiments in Haake Mini Lab 2 are limited to a sample size of about 5-7 g PP granules. Experiments were up-scaled to an Extron Ex-18-25-1.5 single screw extruder with 18 mm screw diameter and L/D of 25:1, two heating zones and the die (Figure 39).

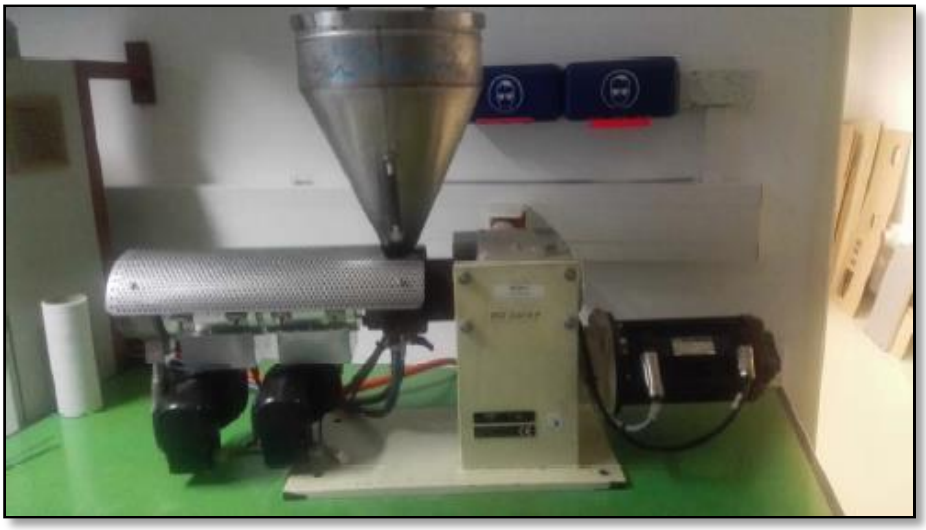


Figure 39: Extron EX-18-25-1.5 Lab Extruder

As temperature in first heating zone (feeding zone) 170°C was chosen, in the second heating zone 200°C and the die temperature was 200°C. Screw speed was 50 rpm.

3.2.3. Specimen preparation

3.2.3.1. Tensile tests and impact tensile test

The specimen for the tensile tests and the impact tensile tests were injection moulded using a Haake Mini Jet 2. The cylinder temperature was 230°C and the mould was heated to 80°C (the moulds are shown in Figure 40). The injection pressure was 500 bar. Tensile test specimens were prepared according to DIN 527-2 type 5A [7]. The geometry of the impact tensile test specimens was 60 mm x 10 mm x 1 mm. Samples were notched and tested according to DIN 8256 method A [8].

Figure 40: Geometry of the moulds

3.2.3.2. Rheological tests

Discs with 25 mm diameter and 1.2 mm thickness for dynamic rheology and sheets with 100 mm x 100 mm x 0.5 mm for extensional rheology were compression moulded at 25 bar and 180°C. As heating and cooling rate of the laboratory press 25 K/min was chosen.

3.2.4. Analytical methods

3.2.4.1. Tensile test and impact tensile test

The test machine (Zwick 050) was equipped with an extensometer and 1 kN load cell, the test speed was 10 mm/min. The notched impact tensile test specimen were tested on an Instron CEAST 9050 impact pendulum (2 J hammer; cross head mass = 15 g). The tests were performed according to the corresponding standard [7] and [8].

3.2.4.2. Differential Scanning Calorimetry (DSC)

Approximately 5 mg of the polymer sample were used for DSC-analysis. The sample was weighed in TA standard aluminium pans, sealed and measured on a TA Q2000 DSC. Samples were heated to 200°C with 10 K/min to eliminate the thermal history, then cooled down to room temperature (10 K/min) and heated up again to 200°C (10 K/min). TA Universal analysis software was used to determine melting (T_m) and crystallisation temperature (T_c), as well as the melting enthalpy (ΔH_m).

3.2.4.3. Oxidation induction time (OIT)

OIT was determined according to DIN 11357-6 [9]. The samples were heated in open pans to 200°C (10 K/min) under nitrogen atmosphere. Then the purging gas was changed to air and the temperature was kept at 200°C for 90 min.

3.2.4.4. Gel content

The gel content was determined based on ASTM D 2765 [10]. 300 mg of the polymer were weighed into paper filters and refluxed in a 250 ml flask in 100 ml xylene under argon for 24 hours. To prevent thermal degradation Irganox 1010 was added to the solution.

3.2.4.5. Molar mass determination

The determination of the molar mass distribution (MMD) was carried out on a Viscotek High Temperature size exclusion chromatography (HT-SEC) system at 140°C with

1,2,4-trichlorobenzene as eluent and standard triple detection (refractive index, low angle light scattering and capillary viscometer). The device was calibrated with PE standards. The experiments were performed at the Institute of Polymer Chemistry at Johannes Kepler University Linz. MMD was determined from the refractive index detector signal. Data from the capillary viscometer were used for the Mark-Houwink plot to calculate the degree of branching according to the model of Zimm-Stockmeyer. The ratio of the mean square radii of gyration g was calculated from the intrinsic viscosity of the branched $[\eta]_b$ and the linear $[\eta]_l$ polymer with equation 5. For LCB-PP a value of $\epsilon = 0.75$ was used according to literature [3, 11].

$$g = \left(\frac{[\eta]_b}{[\eta]_l}\right)^{\frac{1}{\epsilon}} \tag{5}$$

The degree of branching B_n was calculated using equation 6:

$$g = \left[\left(1 + \frac{B_n}{7}\right)^{\frac{1}{2}} + \frac{4B_n}{9\pi}\right]^{-\frac{1}{2}} \tag{6}$$

3.2.4.6. *Dynamic rheology*

Dynamic rheology measurements were carried out on a Plate-Plate Anton Paar MCR 301 rheometer equipped with CTD 450 heating chamber under nitrogen at 180°C with 1 mm gap size. Frequency was chosen between 628-0.01 rad/s, deformation was raised from 1-2% logarithmically during the measurement. Deformation was in the linear viscoelastic range, which was checked by amplitude sweep. Thermal stability over time was proven by a time sweep over 2 h at constant conditions. The zero shear viscosity η_0 of the linear samples was calculated using equation 7, the simplified model of Carreau-Yasuda for polymer melts [12, 13].

$$\eta(\dot{\gamma}) = \frac{\eta_0}{[1 + (\lambda \cdot \dot{\gamma})^{\alpha}]^{\frac{1-n}{a}}} \tag{7}$$

This model uses the relaxation time λ, the power law index n and the “Yasuda-exponent” α. The calculation was performed automatically by the delivered Anton-Paar-software package. The software offers further fit-functions for the calculation of η_0, the model of Carreau-Yasuda gave the best fit for the performed frequency sweeps.

The zero-shear viscosity η_0 of the branched samples was determined by measuring the creep compliance at 180°C and a constant stress τ of 5 Pa and 30 Pa. For small stresses, there exists a linear range, where the creep compliance $J(t,\tau)$ reaches a stationary state and the zero shear viscosity η_0 can be taken from the plateau of t/J (equation 8).

$$\eta_0 = \lim_{t\to\infty}\left(\frac{t}{J(t,\tau)}\right) \tag{8}$$

3.2.4.7. *Extensional rheology*

Stripes with 8 mm width for extensional rheology were cut from 100 mm × 100 mm × 0.5 mm sheets after compression moulding at 180°C. Extensional rheology was measured using a Sentmanat Extensional Rheometer (SER-HPV 1) for Anton Paar rheometers, at 180°C and five different strain rates ($\dot{\varepsilon}$ = 10 s^{-1}; 3 s^{-1}; 1 s^{-1}; 0.3 s^{-1}; 0.1 s^{-1}). Start-up curve was measured with a steady shear experiment with a plate-plate system and two different shear rates (0.001 s^{-1} and 0.1 s^{-1}). The strain hardening ratio X_e was calculated using equation 9 and the maximum value of the elongational viscosity η^+_{Emax} for every strain rate and the corresponding value from the linear viscoelastic start up curve [6].

$$X_e = \frac{\eta^+_{Emax}(t,\dot{\varepsilon})}{\eta^+_{LVE}(t)} \tag{9}$$

Due to internal friction of the SER-tool the measured SER curves needed to be adapted to the threefold of the linear viscoelastic start up curve.

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4. Results and discussion

4.1. Long chain branching of single polymer PP

4.1.1. Preliminary experiments

First preliminary experiments were performed according to Su et al., who used dicumyl peroxide to initiate LCB reaction and a trifunctional monomer trimethylolpropane-triacrylate (TMPTA) for radical stabilisation and branching [1]. A high temperature stable organic peroxide 2,5-bis(tert-butylperoxy)-2,5-dimethyl-hexane (trade name Peroxan HX or Luperox 101) was used instead of dicumyl peroxide, because of its better compatibility with PP, its safe handling and because it is less hazardous to health [2]. Acrylates are common monomers for PP modification, but they are polar and show weak miscibility with PP in melt [3]. To improve the efficiency of the LCB reaction with TMPTA, Zhang et. al added co-agents like dithiocarbamates (sulphur based chain transfer agents) [4]. Similar results are also reported with tetramethyl piperidineoxyl (TEMPO) as co-agent – the stable radical of the hindered amine tetramethyl piperidine [5, 6]. Hindered amine light stabilisers (HALS) also have the tetramethyl piperidine functional group. This could offer the possibility to use a standard plastic additive as co-agent for LCB-reaction. This would enable a cost effective process, which is beneficial in recycling business. Therefore, first experiments were performed with TEMPO as co-agent for LCB.

A combination of 5 mmol/kg Peroxan HX with 125 mmol/kg TMPTA (Figure 41 blue line) was compared with a mixture of 5 mmol/kg Peroxan HX, 125 mmol/kg TMPTA and 6 mmol/kg TEMPO (black line). The samples were prepared according to the described procedure and the structure was characterised by oscillatory rheology. The results from frequency sweep are plotted in Figure 41, the red line shows the extruded unmodified, but stabilised PP3. Without TEMPO the degradation reaction dominates over recombination (blue line), after adding TEMPO the viscosity is increased significantly (black line). However, the modulus crossover point of the black line does not significantly shift compared to the red line. A second elastic plateau, which indicates a fraction with very high relaxation times, can be supposed from the curve shape. This is characteristic for a small fraction of polymer chains with very high molar mass.

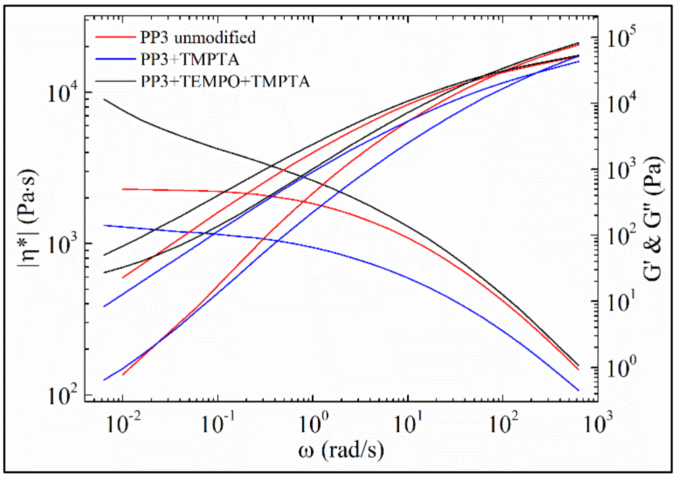

Figure 41: Dynamic moduli and complex viscosity of the preliminary experiments with TMPTA and TEMPO

Consequently, the gel content was determined and showed a xylene insoluble fraction. It was concluded that TMPTA and PP formed small amounts of crosslinked gel and delivered results comparable to Graebling et al. [7]. Compared to the well-defined LCB comb structure of Wang et al. [8] a precise differentiation between crosslinking and branching is not possible, thus this method was proven as unsuitable. After further experiments, the method presented by Wong et al. with the mono-functional monomer styrene was chosen for LCB to exclude crosslinking [9].

4.1.2. LCB with styrene and peroxide *(Paper I)*

Wong et al. proposed LCB for some of their styrene grafted PPs, but they did not optimise the conditions for an intended LCB reaction. Therefore, several experiments with virgin grade PP (PP3) were performed in this study. The concentration of peroxide was taken from Wong et al. with 20 mmol/kg and the amount of styrene was varied. The ideal molar ratio of radicals (one mole Peroxan HX generates in average three mole radicals [10]) and double bonds (one mole double bonds per mole styrene) was found to be $c_{radicals}:c_{styrene}$ = 1:8 (20mmol/kg Peroxan HX and 480 mmol/kg styrene). The criteria for optimisation compared to the linear pre-cursor were a higher complex viscosity in the area of low shear and shear thinning at higher frequencies. These changes of the rheological behaviour after chemical modification are well known for a branched structure [11]. With higher amounts of styrene (ratio 1:12 and

1:16), these effects intensify. According to Wong et al., depending on the amount on chemically bonded styrene to PP recombination takes place. Furthermore, they predicted a stepwise change of the flow properties depending on the degree of grafting: First, complex viscosity $|\eta^*|$ decreases (as a result of chain scission and grafting), then long chain branching takes place (recombination of PP-g-styrene fragments starts). However, this turns into cross-linking if higher amounts of styrene are used [9]. The results with 5 different ratios of radical:styrene with constant amounts of peroxide are shown in Figure 42, which are in accordance with the results of Wong et al..

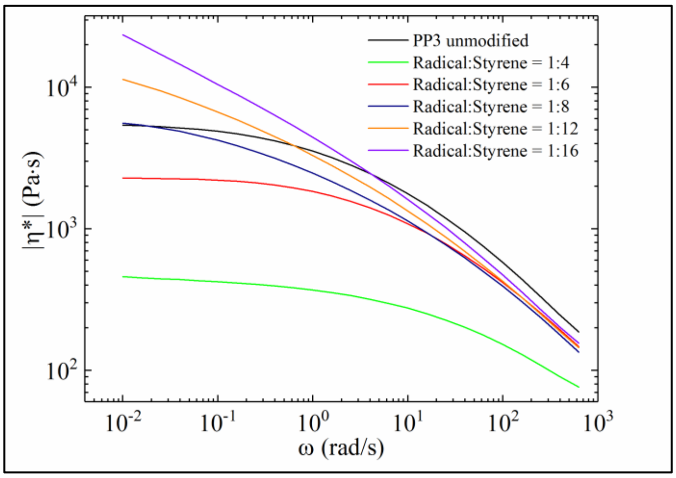

Figure 42: Comparison of the complex viscosity of LCB PP with different radical:monomer ratios

A second mixture with more peroxide and more styrene was chosen (35 mmol/kg Peroxan HX and 840 mmol/kg styrene; A2). It is expected that more peroxide and more styrene result in a higher average number of branches per molecule. The ratio of radicals and styrene was again 1:8 to prevent degradation. The designation of the mixtures is given in Table 9 in section 3.2.1.1. The sample names are a combination of the polymer name and the mixture designation (e.g. PP3 modified according to method A1 is named PP3A1).

PP3 was long chain modified using mixtures A1 and A2. Figure 43 shows the dynamic viscosity curves and the extensional viscosity curves thereof. Linear unmodified PP3 (black line) reaches the zero shear viscosity plateau (η^0) already at $\omega > 0.01$ rad/s and shows no strain hardening behaviour. Modified samples PP3A1 (blue line; 20 mmol/kg Peroxan HX and 480 mmol/kg styrene)) and PP3A2 (green line; 35 mmol/kg

Peroxan HX and 840 mmol/kg styrene) show a broader transition from power law to the zero-shear viscosity regime. This transition becomes the broadest in case of PP3A2. Furthermore, the absolute value of the complex viscosity $|\eta^*|$ becomes highest in the low frequency area and pronounced shear thinning at high ω is shown. The modulus crossover points (crossover modulus $G' = G'' = G_c$ and crossover frequency ω_c; given in Table 10) of PP3A1 shifts to higher ω_c (M_w decreases), but lower G_c (MMD broadens). ω_c of PP3A2 is shifted to lower frequencies (M_w increases) and G_c decreases slightly (MMD broadens) [12, 13].

Table 10: Modulus crossover points of linear and LCB samples

	G_c [kPa]	ω_c [rad/s]
PP3	27.0	41
PP3A1	23.0	83
PP3A2	15.7	39

According to the results of the extensional rheology in Figure 43 (right), both modified samples show strain hardening. The strain hardening ratio (X_e) decreases with decreasing strain rate (in contrast to WE100HMS, the industrial film blowing HMS-PP) and is more pronounced for PP3A2. According to Gabriel et al. a pronounced strain hardening at higher strain rates can be a hint for more long chain branches per polymer chain [14].

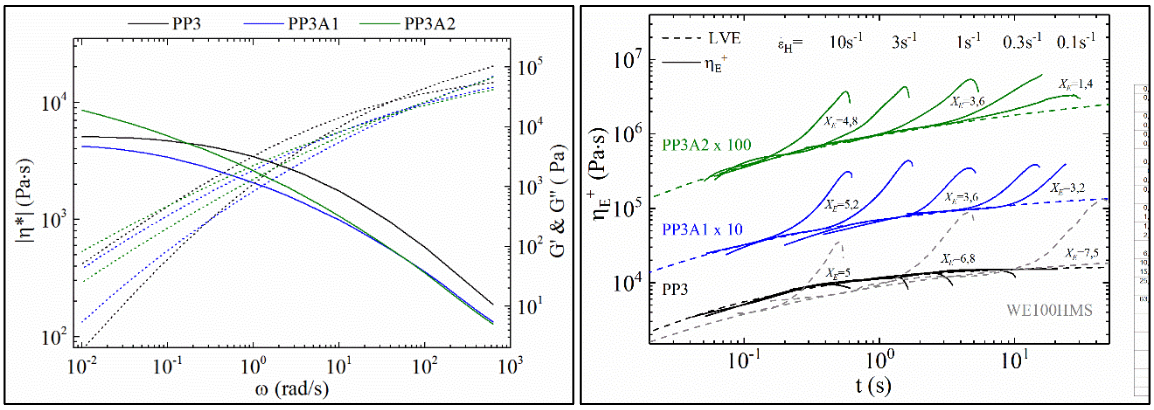

Figure 43: Dynamic rheology curves (left) and extensional rheology (right) of styrene and peroxide modified PP3, the SER-curves of PP3A1 and PP3A2 are shifted.

Grafting reactions often go hand in hand with degradation and therefore an increase of the tensile modulus and a decrease of elongation at break [15]. Similar effects are also reported for LCB-PP from electron beam irradiation by Yoshiga et al. [16] and from an industrial branched PP [17]. Figure 44 shows the tensile modulus and elongation at break results from tensile tests, furthermore the impact tensile strength is depicted. PP3A1 and PP3A2 show that modification with styrene reduces the tensile modulus at first and increases it again with a higher amount of styrene and peroxide (but within the error tolerances). Elongation at break and the impact tensile strength decrease with higher concentration of styrene and peroxide compared to the unmodified material. The brittleness and low elongation at break of the styrene-modified samples can be explained by the rigidity of the modified amorphous phases caused by introduced polystyrene side chains [18].

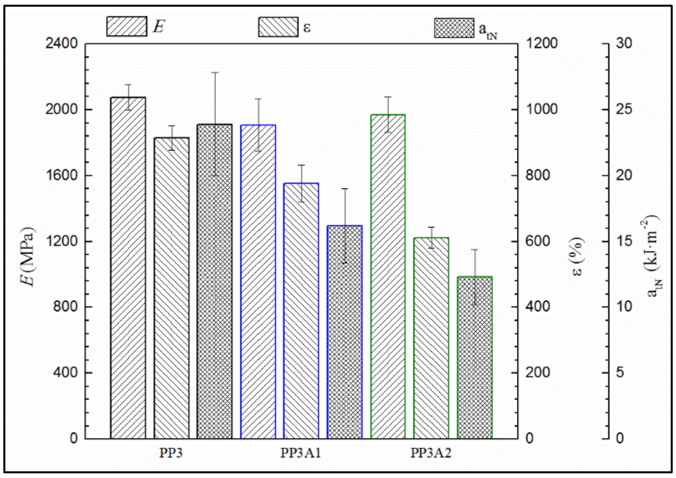

Figure 44: Results from tensile and impact tensile tests of styrene and peroxide modified and unmodified PP3

The melting temperature T_m and the melting enthalpy ΔH_m lower and therefore the crystallinity decreases slightly with higher styrene and peroxide content (see appendix), but the crystallization temperature T_c increases (see Figure 45). The grafted polystyrene chains cannot form crystalline parts and remain in the amorphous phase (reduction of T_m and ΔH_m), but they can improve the nucleation of the crystallisation of the PP (increase of T_c) [9, 19].

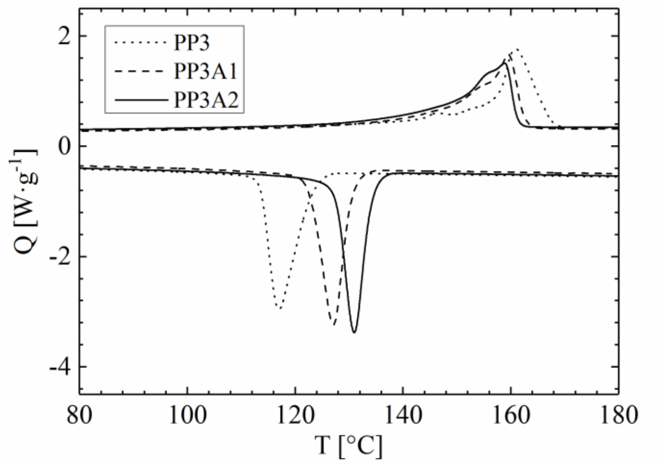

Figure 45: Comparison of the DSC curves of PP3, PP3A1 and PP3A2

4.1.3. LCB with PODIC *(Paper I)*

Additionally to the LCB by peroxide assisted melt grafting of styrene, LCB with peroxydicarbonates (PODIC) with long aliphatic chains according to the work of Lagendijk et al. using 20 mmol/kg di-myristyl-peroxydicarbonate (mixture designation B; PP3B) was performed [20]. Similar to PP3A1, PP3B shows a broader transition from power law to zero shear viscosity and a lower value of η_0 compared to the linear PP3 indicates chain scission. The modulus crossover point of PP3B (ω_c = 87 rad/s and G_c = 25 kPA) also indicates a decrease of molar mass, but slight broadening of MMD compared to PP3 (ω_c = 41 rad/s and G_c = 27 kPA). The modification with PODIC also introduced strain hardening to the sample and pronounced strain hardening at lower strain rates was obtained, contrary to the results of PP3A1 and PP3A2 (Figure 46). The strain hardening ratio of PP3B is quite near to the industrial film blowing HMS-PP WE100HMS.

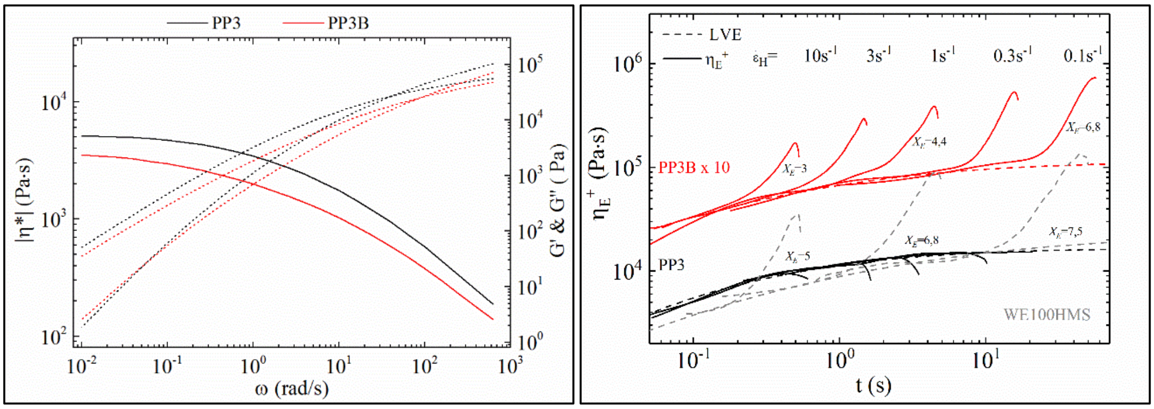

Figure 46: Dynamic rheology curves (left) and extensional rheology (right) of PODIC modified PP3, the SER-curve of PP3B is shifted by a factor of 10.

The modification with PODIC reduces the tensile modulus of PP3B and increases the elongation at break slightly (Figure 47) compared to PP3. The impact resistance was reduced. Overall, PODIC modification results in some kind of softening of the material. This can be explained by the formation of LCB and the aliphatic residuals from PODIC (myristic acid or alcohol), which have a plasticizing effect.

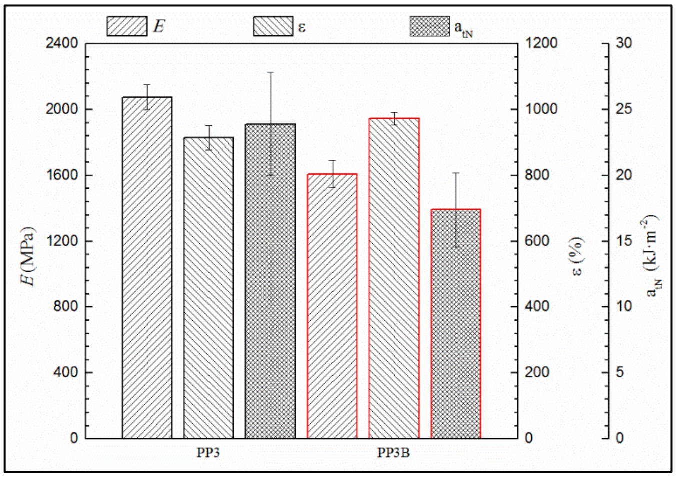

Figure 47: Results from tensile and impact tensile tests of PODIC modified PP3B and unmodified PP3

Compared to PP3A1, T_c of PP3B shifts to higher values and additionally the crystallisation peak narrows significantly (Figure 48). Contrary to the styrene-grafted samples, T_m and ΔH_m rise little (see appendix). The improved crystallisation of LCB-PP is controversially discussed in literature. On the one hand, branches should reduce crystallinity, but on the other hand, results showed that small amounts of LCB improve the nucleation ability and increase crystallinity [21]. A point of contention are residuals from the used co-agents for the LCB reaction that can act as nucleation agent (e.g. benzoic acid from benzoyl peroxide) [22]. Since the decomposition products of PODIC are still liquids at T_c, nucleating effects may be excluded. So, the risen T_c,T_m and ΔH_m, as well as the narrowed crystallisation peak (in combination with the results from rheology) favour rather the theory that small amounts of LCB increase crystallinity.

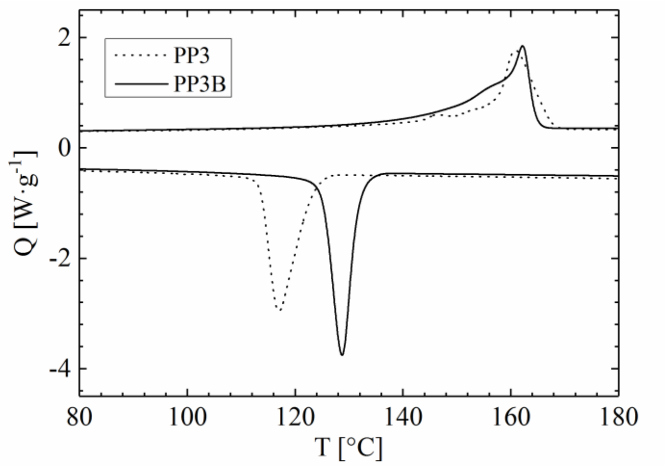

Figure 48: Comparison of the DSC curves of PP3 and PP3B

4.1.4. LCB of recycled single polymer PP *(Paper II)*

The following experiments are always compared with casting grade PP3, since the recycled materials rPP and mBlend have comparable molecular parameters.

The procedures (20 mmol/kg peroxide + 480 mmol/kg styrene A1; 35 mmol/kg peroxide 840 mmol/kg styrene A2; 20 mmol/kg di-myristyl-peroxydicarbonate B) presented in the section before were repeated with post-consumer PP from recycled thermoformed cups (rPP) produced from PP-homopolymer.

As expected rPP shows no strain hardening and has a slightly higher zero shear viscosity than PP3 (Figure 49 left). Long chain branching gave the same trends (G_c ↓; ω_c ↑) for rPP as for PP3. The LCB modification reduces $|\eta^*|$ at higher ω (shear thinning behaviour) and the transition from power law to η^0 regime becomes broader and zero-shear viscosity increases. In addition, the shift of the crossover modulus and the crossover frequency shows the same trends. However, rPPB, styrene and peroxide modified rPPA1 and rPPA2 show strain hardening in elongational flow (Figure 49 right).

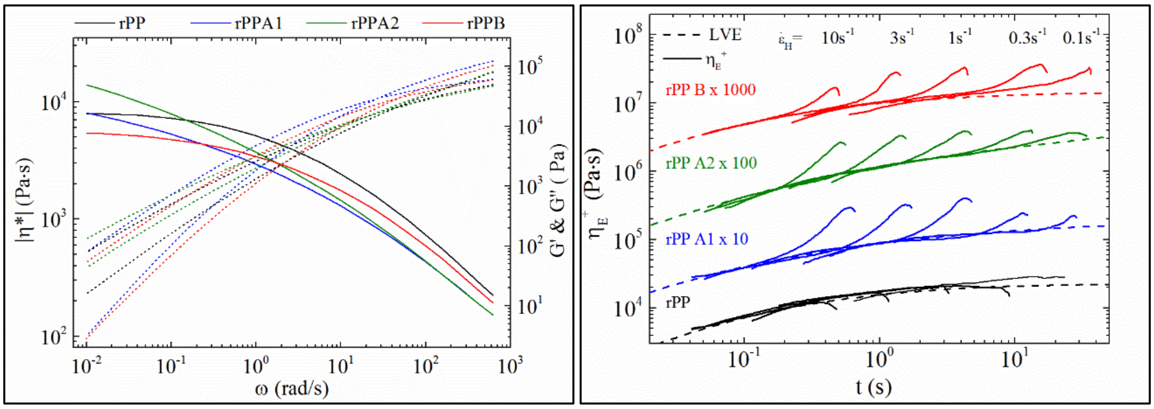

Figure 49: Dynamic rheology curves (left) and extensional rheology (righ(of chemically modified recycled PP. The SER curves of the modified samples are shifted by the given factors.

Furthermore, rPPA1 and rPPA2 have strain rate dependencies (Figure 50) similar to PP3A1 and PP3A2, but rPPB differs from PP3B and shows no pronounced strain hardening at lower strain rates.

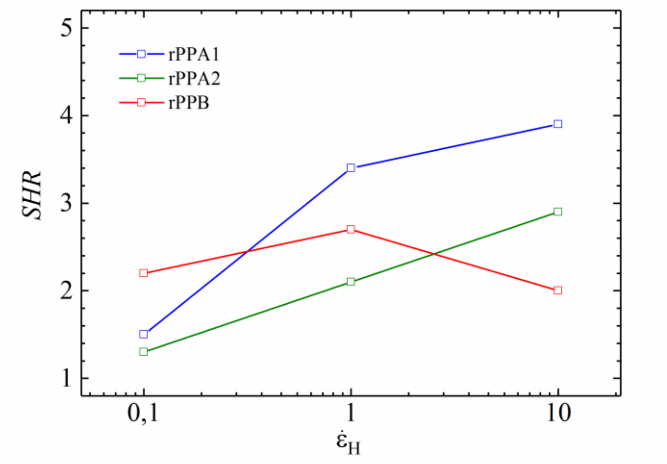

Figure 50: Strain hardening ratios of the rPP samples

The tensile tests in Figure 51 show a good improvement of the elongation at break in the case of PODIC modified rPPB. However, modification with styrene reduces the elongation at break (rPP1). This effect intensifies with a higher content of additives (rPPA2). The trend of the tensile modulus curves is comparable to PP3A1, PP3A2 and PP3B and the smallest values for the tensile modulus were obtained with PODIC for LCB in rPPB. The impact tensile strength of rPPA1 and rPPA2 is dramatically reduced and less than half of a_{tN} of rPP. a_{tN} of rPPB is slightly reduced, but within the fluctuation range of rPP. All in all, these results are in accordance with the model experiments with virgin PP.

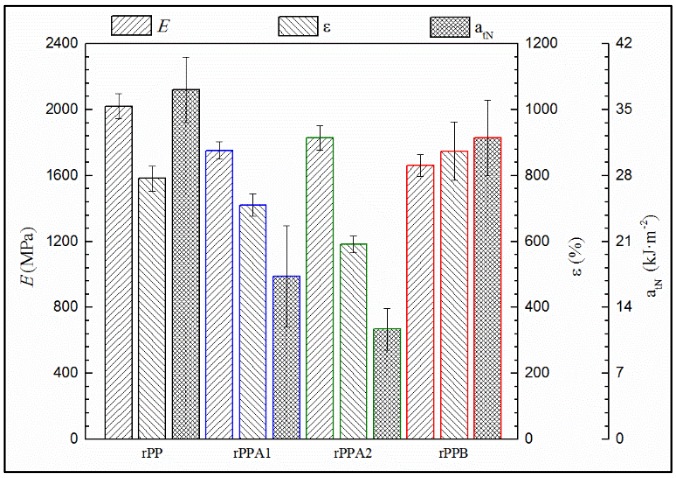

Figure 51: Results from tensile and impact tensile tests of modified and unmodified rPP

4.2 Influence of 10% PE-HD on LCB of PP

4.2.1. Model mixtures *(Paper I)*

Figure 52 shows the viscosity curves of mBlend and the structurally modified blends. mBlendA1, mBlendA2 and mBlendB show changes of $|\eta^*|$ similar to the single polymer sample in Figure 43 and Figure 46 and the curves have a similar shape.

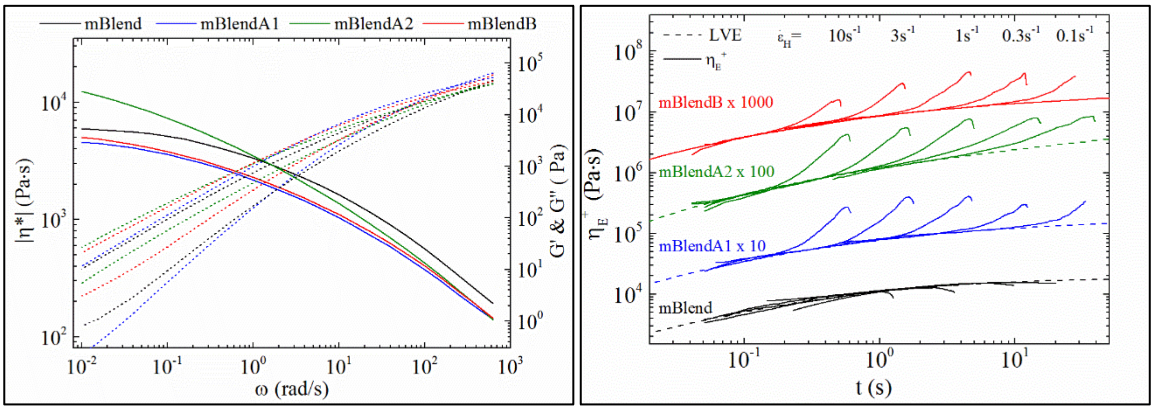

Figure 52 Dynamic rheology curves (left) and extensional rheology (right) of chemically modified model blends. The SER curves of the modified samples are shifted by the given factor.

The crossover point (Table 11) of mBlendA2 shifts to lower ω_C compared to PP3A2 and $|\eta^*|$ at ω = 0.01 rad/s has a higher absolute value, which can be a hint for a higher molar mass. Also mBlendB shows changes similar to PP3B.

Table 11: Modulus crossover points of linear and LCB blends

	G_c [kPa]	ω_c [rad/s]
mBlend	29.0	53
mBlendA1	24.0	83
mBlendA2	16.0	26
mBlendB	26.0	85

mBlend shows the same behaviour of extensional viscosity as PP3. It is pointed out that after modification a significant amount of gel was formed in mBlendA1 and mBlendB (Table 12). In case of mBlendA2 the gel content is significantly lower than in mBlendA1, thus higher amounts of chemicals reduced crosslinking. Obviously, the PE-HD undergoes crosslinking as side reaction during radical modification. It is well known that PE tends to crosslink during radical induced grafting, while PP degrades [23]. Styrene should reduce degradation as well as crosslinking. Mixture A1 is not suitable to reduce crosslinking sufficiently, but A2 is. It must be noted that crosslinked structures can also cause strain hardening, especially crosslinked PE (e.g. strain hardening in PE-LD) [24]. To compare the strain hardening of the model mixtures, the strain hardening ratio is depicted in Figure 53 (left). Additionally, the extensional viscosity of PP3B, mBlendB and mBlendB after gel removal are plotted against the Hencky strain ε in Figure 53 (right).

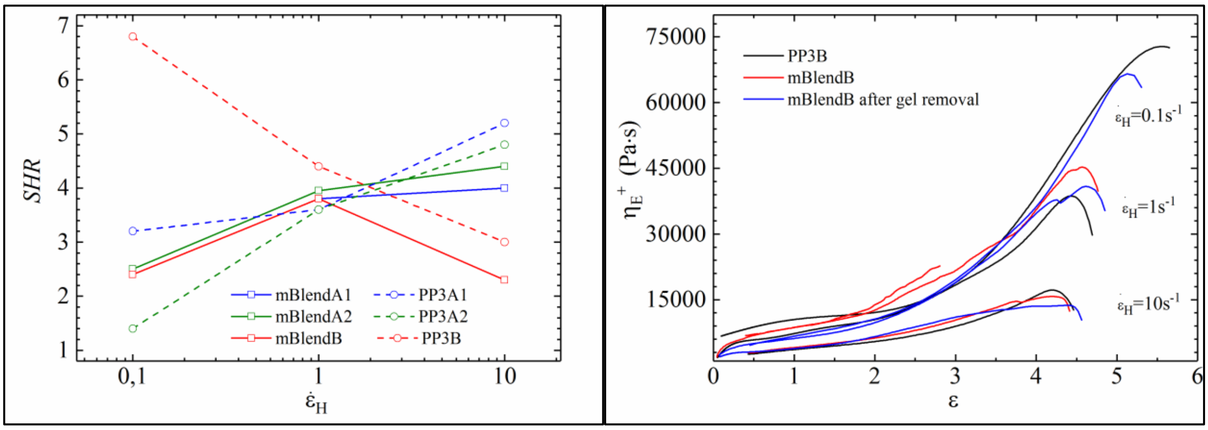

Figure 53: Strain hardening ratios against the strain rate (left) and the extensional viscosity against the strain (righ

mBlendA1 and mBlendA2 show nearly the same strain hardening behaviour, while PP3A1 and PP3A2 differ in their dependency of the strain hardening on the strain rate. mBlendB cannot compete with strain hardening of PP3B at low strain rates, however, at higher strain rates the strain hardening ratios get closer. If the gel content of mBlendB is removed, also the strain hardening at low strain rates becomes similar to PP3B.

Table 12: Gel contents of mBlend samples

Sample name	Gel content [%]
mBlend	0
mBlend A1	12.9 ± 2.5
mBlend A2	1.5 ± 2.8
mBlend B	15.3 ± 2.3

Although a significant amount of xylene insoluble gel in case of mBlendA1 and mBlendB was formed, which affects the elongation at break significantly. However, mBlendB shows an unexpected behaviour in mechanical testing (Figure 54). Interestingly, the impact tensile strength of mBlendB increased to 27 kJ/m^2 after modification, which is almost twice the value of mBlend and 10 % more than unmodified PP3. mBlendA1 does not show such an increase in impact tensile strength, despite of a similar gel content compared to mBlendB.

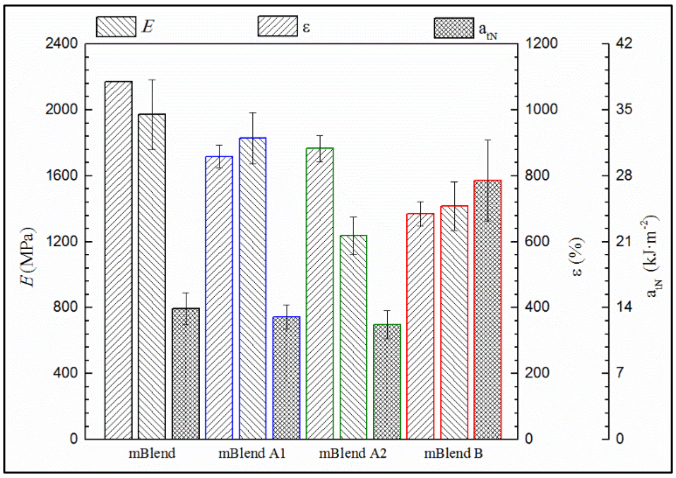

Figure 54: Results from tensile and impact tensile tests of modified and unmodified mPP

To provide clarification, SEM micrographs of the fracture surfaces were taken after cryo treatment. In Figure 55 on the left side unmodified mBlend is shown and a finely dispersed morphology of PE in PP can be seen. Modification with PODIC increases the size of some of the particles, which can be also seen from the particle size distribution in the left bottom corner of the micrographs.

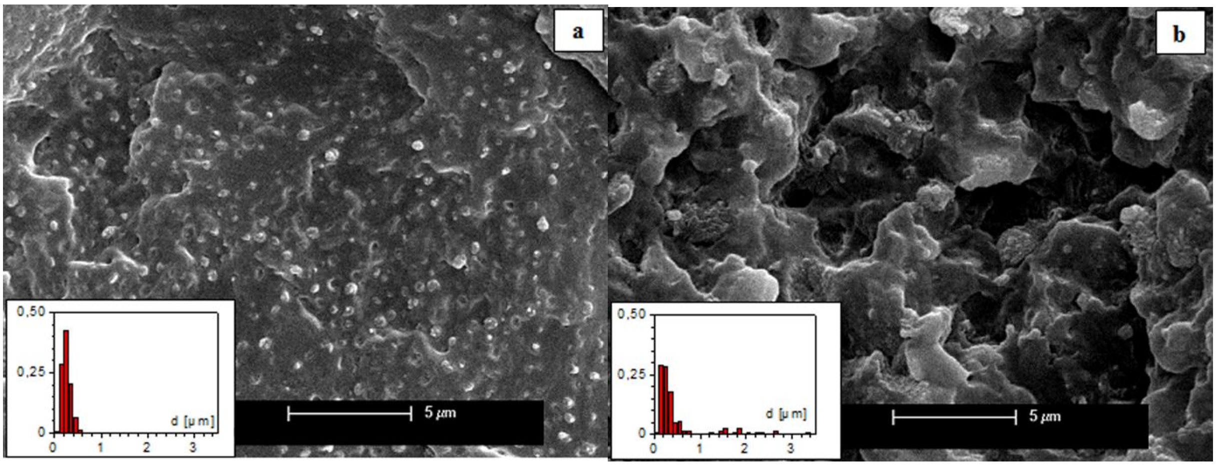

Figure 55: SEM Micrographs of the cryo fracture surfaces of mBlend (a) and mBlendB (b)

The surface of mBlendB shows plastic deformation (despite the cryo treatment) and looks less stiff than mBlend. Literature offers some explanations for an increasing impact resistance of peroxide treated PP/PE-blends [25], but such toughening is not reported for PODIC. Therefore, further investigations seem promising and will be part of future research.

4.2.2. Recycled post-consumer waste blend *(Paper II)*

rBlend consists of different PP- and PE-HD-grades. The complex viscosity and dynamic moduli of the raw materials are given in Figure 56. The rheology data are within the expected range of the different fields of application. The recycled blow moulded PE-HD shows the highest complex viscosity, the injection moulded PP the lowest at small and at high frequencies. This must be considered by evaluating the results from mechanical testing.

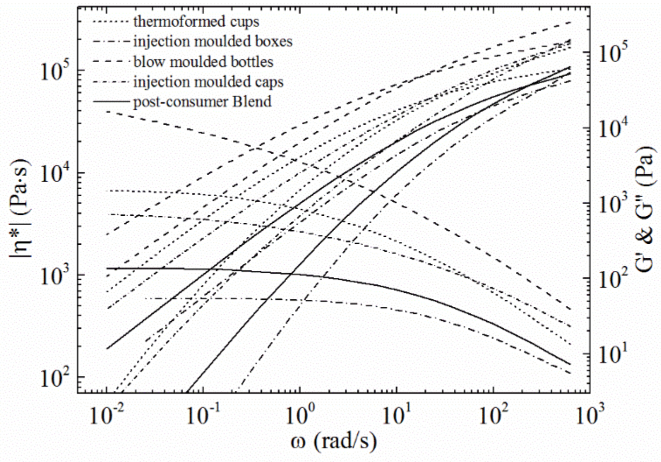

Figure 56 Rheology curves of the single components for rBlend

rBlend was branched according to the given procedures. As expected and comparable to mBlendA1 and mBlendB, rBlendA1 and rBlendB formed significant amounts of xylene insoluble gel particles (Table 13). However, comparable to mBlendA2, modification also did not form xylene insoluble gel particles in rBlendA2.

Table 13: Gel contents of rBlend samples

Sample name	Gel content [%]
rBlend	2.5 ± 1.4
rBlend A1	13.1 ±2.5
rBlend A2	0
rBlend B	10.5 ± 3.8

The rheology curves are shown in Figure 57. $|\eta^*|$ of rBlend reach the zero shear viscosity η_0 under the given conditions. PE in a PP/PE-blend or in a PP/PE-copolymer can form highly branched networks during peroxide assisted chemical modification, which are insoluble in boiling xylene. Such networks can cause a second elastic plateau, which can be highlighted as second crossover point of the moduli and are proven by gel content determination (Table 13). It is noted that the unmodified sample rBlend showed no strain hardening, but significant sagging of the polymer stripe. Due to its low zero shear viscosity it was not possible to determine $\eta^{+}{}_{E}$ at strain rates below $\dot{\varepsilon} = 3\,\mathrm{s} - 1$. Both styrene modified samples show strain rate dependent strain hardening which is more pronounced at high than at low elongation rates. The PODIC modified sample rBlendB shows strain hardening, but no strain rate dependency like mBlend from virgin material.

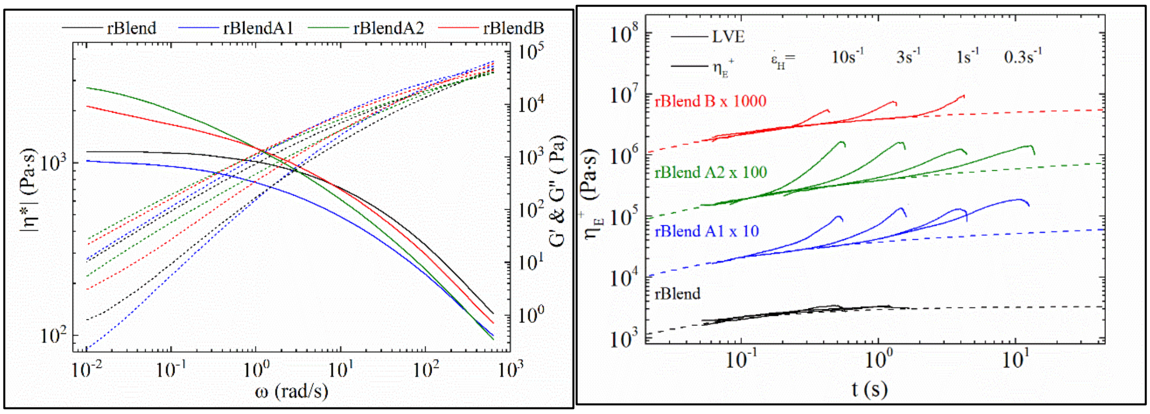

Figure 57 Dynamic rheology curves (left) and extensional rheology (right) of chemically modified recycled blends. The SER curves of the modified samples are shifted by the given factors.

Concerning the mechanical properties depicted in Figure 58, all rBlend samples showed a weak. The measured elongation at break was far below the expectations. The trend of the tensile modulus curves is similar for both feedstock materials and the smallest values for the tensile modulus were obtained with PODIC for LCB.

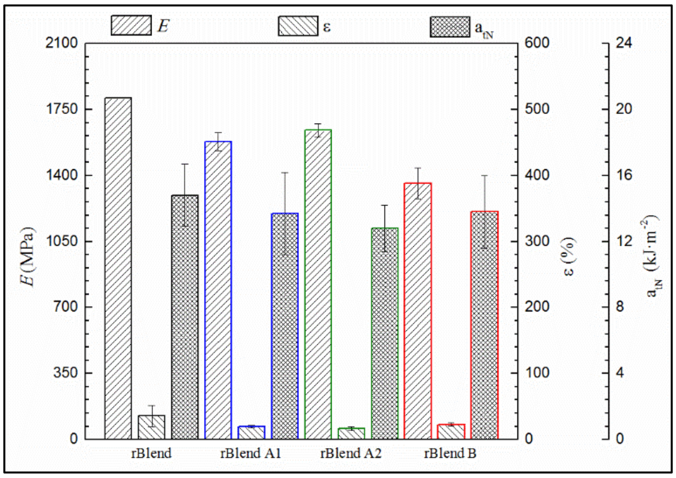

Figure 58: Results from tensile and impact tensile tests of modified and unmodified rPP

The formed gel is expected to cause a significant deterioration and some dispersed PE-HD particles can be already seen by eye without any magnification, which is shown in

Figure 59. Due to the unfavourable ratio of matrix and dispersed phase viscosity, the dispersed PE-HD influences the morphology and the mechanical properties negatively. According to Wu, the size of the drops of the dispersed phase is directly proportional to the ± 0.84 power of the viscosity ratio [26]. The drops are smaller when the ratio is closer to unity. This requirement could not be fulfilled with the composition of rBlend.

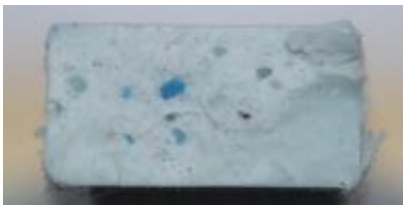

Figure 59: Fracture surface of the rBlend from tensile test

4.3. Influence of stabilisers on LCB of different PP grades

From literature it is known that stabiliser-systems – especially hindered amine light stabilisers and sulphur containing additives – can influence the melt modification of PP [5]. Therefore, the oxidation induction time (OIT; performed according to DIN 11357-6) of the different polypropylene types was determined to compare the stabiliser effectiveness of the materials [27]. Especially concerning recycling of post-consumer waste different amounts of active and inactive stabiliser must be considered. The OIT method is a good possibility to compare the stabiliser activeness under thermo-oxidative conditions, but has limitations that always must be considered. Especially PP1 for pipes and PP4 for injection moulding are expected to have a higher content of active stabiliser, because they are designed for long-term applications. PP2 for thermoforming and PP3 for film casting and chill rolling are designed for short life applications like packaging material and the stabiliser content is expected to be lower.

According to the producer [28], following additives are known for the used PP’s (unfortunately no further information can be given because of intellectual property reasons):

Table 14: Additive composition in the different virgin PP grades

	Heat stabilisers Irganox 1010	Process stabiliser (Irgafos 168)	Acid Scavenger Calciumstearate	Thiosynergist (Lowinox)	Antistats Glycerol-monostearate
PP1	X	X	X	X	X
PP2	X	X	X		
PP3	X	X	X		
PP4	X	X	X	X	X

A verification of the assumptions is shown in the OIT curves of the virgin PPs and are given Figure 60. As expected, PP1 and PP4 had an OIT longer than 90 min, while PP2 and PP3 degrade under the same conditions. To study the effect of the molar mass on LCB, the stabilisers had to be washed out of the grinded polymers. PP1, PP2 and PP3 were treated by soxhlet-extraction with acetone over night. In case of PP4 it was necessary to repeat the procedure with dichloromethane, since OIT showed residual stabiliser content. After this procedure, OIT of all samples was below 10 min and side effects of the stabilisers are expected to be minimised.

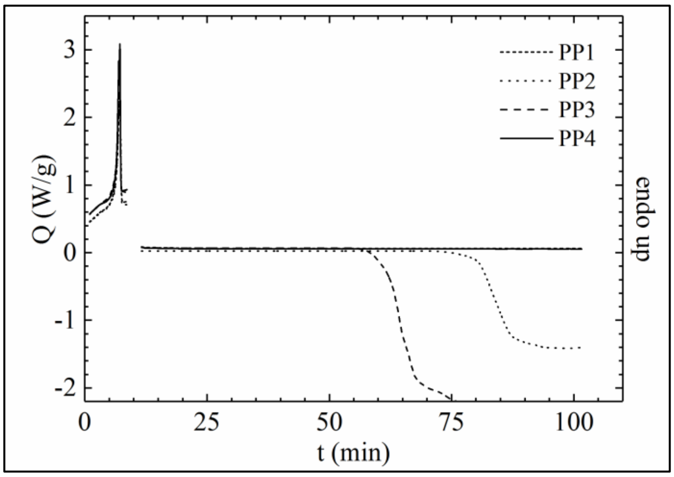

Figure 60: OIT curves of the virgin grade PP granules

The extracted polymer powders have been dried in vacuum at 40°C to remove the solvent and were chemically modified using the method with PODIC. For comparison also fully stabilised polymers were long chain branched with PODIC. The dynamic rheology curves of the samples are given in Figure 61. The results are equivocal: Interestingly, the stabiliser cocktail of PP4 does not influence the modification and complex viscosity, PP4B and extr. PP4B are similar. In case of PP1 and PP2 the stabiliser cocktails seems to be beneficial for modification as complex viscosity at low shear is higher compared to the extracted samples. On the other side for PP3 the opposite occurs, the removal of the stabiliser seems to be beneficial. However, it can be concluded, according to the results of the extracted polymer samples, that a comparable increase of $|\eta^*|$ at low frequencies occurs and no confounding effects of stabilisers take place.

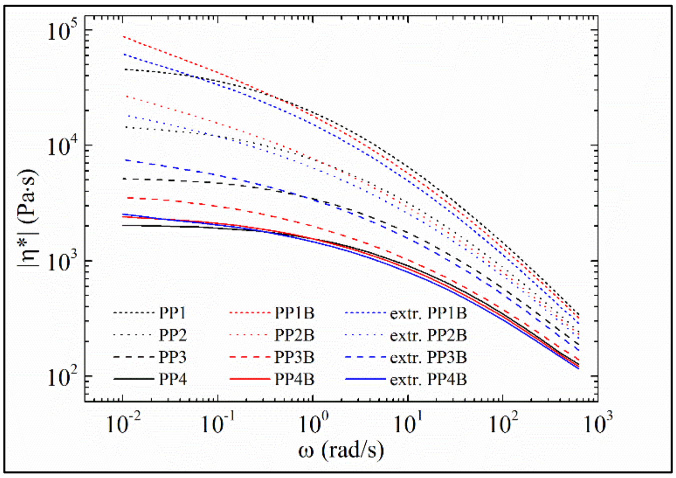

Figure 61: Comparison of the dynamic viscosity of the polymer samples using PODIC before and after removal of the stabiliser cocktail

Overall concluded, it is necessary to know the class of stabilisers (functional group), the concentration (depends on manufacturer) and the content of active stabiliser (depends on the history of the material). This will be a crucial topic to develop a reliable recycling concept in future.

4.4. Influence of the molar mass on LCB of PP *(Paper III)*

To exclude side effects from the stabiliser systems the influence of the molar mass of the linear PP precursor will be discussed using the extracted PP samples. Furthermore, only LCB samples prepared with the PODIC will be used, because the branching mechanism is simpler. The LCB according to Wong et al. depends on an efficient grafting of styrene onto PP in the first step and then in a successful recombination in a second step. A detailed study on the influence of the molar mass on the grafting efficiency of styrene onto PP would exceed the scope of this work.

The dynamic mechanical behaviour of the polymer melts before and after LCB is presented in Figure 62. The addition of LCB affects the elasticity of the melt. The crossover modulus of all samples decreases with LCB (broadening of MMD) and the crossover frequency shifts towards smaller values (higher M_w). With the exception of PP1, its crossover frequency shifts towards a slightly higher value (smaller M_w). All results are in accordance with the data from SEC (Paper III). In the case of PP1, the decreasing molar mass signalises more chain scission during LCB. The linear PP's reach their zero shear viscosity between the frequency 0.1 rad/s and 1 rad/s, while the transition zone from power law to zero-shear regime shifts to smaller frequencies and becomes broader for the LCB-PPs. Further characteristic effects of a branched structure are a pronounced shear thinning at higher frequencies. The effect of shear thinning is more pronounced with PP1-LCB and decreases with diminishing initial molar mass. Additionally, storage modulus of PP4-LCB shows a clear and PP3-LCB shows a slight deviation from the slope of 2 in the low frequency range.

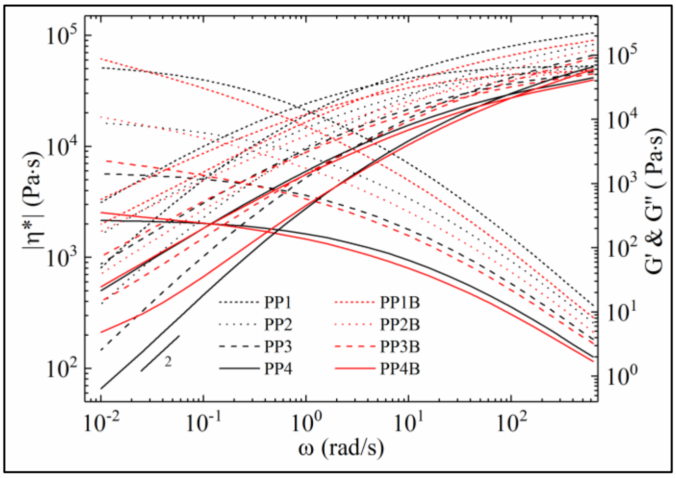

Figure 62: Rheology curves of the extracted PP samples

As can be seen in Figure 63, the linear PPs show no strain hardening behaviour and no deviation from the linear viscoelastic start up curve. Because of the low zero shear viscosity of PP4 at the measuring temperature, it was not possible to measure the extensional viscosity at Hencky strain rates below 1 s^{-1}.

The modification with PODIC induced LCB to the linear polymer backbone and therefore strain hardening behaviour was obtained for all LCB-PPs (Figure 63). According to Gabriel et al. pronounced strain hardening in the low strain rate regime is a hint for a sparsely long chain branched polymer, which is in agreement with the results from HT-SEC and the calculated B_n (average number of branches per molecule). PP2-LCB does not show any strain rate dependence of the strain hardening. In the case of PP3-LCB and PP4-LCB the same behaviour is observed, unfortunately especially at lower strain rates, sagging is in competition with strain hardening.

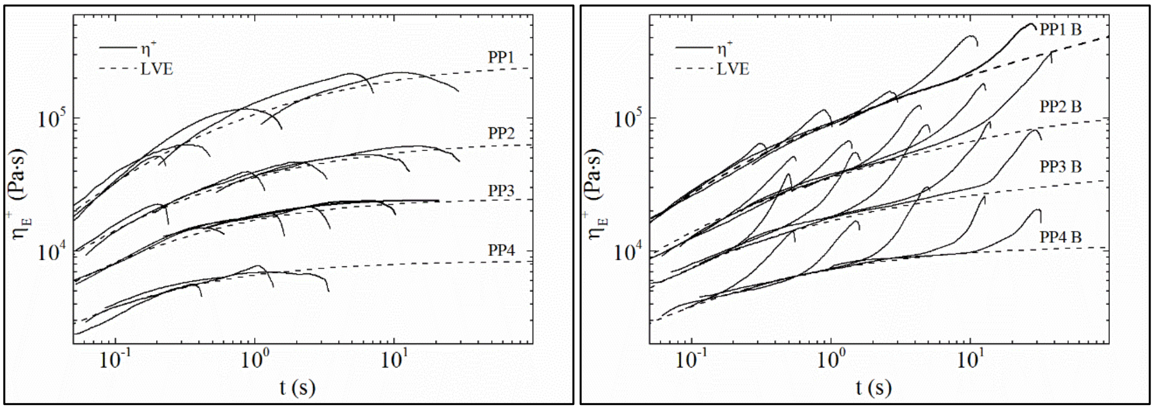

Figure 63 SER curves of the unmodified PP (left) and the LCB PPs (right)

To prove the observations from the extensional rheology measurements the average number of branches per molecule B_n was calculated according to the model of Zimm and Stockmeyer by comparison of the intrinsic viscosity of the branched and the unbranched polymer [29, 30]. A detailed description of the procedure is given in Paper III [31]. The results are given in Table 15 and confirm the suggestions from the extensional rheology. The extrusion type PP1B has a lower branching number compared to injection moulding type PP4B. A possible explanation is reported by Zhu et al.. They employed a chain-length-dependence function and predicted higher rates of termination by combination for shorter chains in polymer melt with free-radical induced cross-linking [32]. If this is applied for this study, the prevalence of LCB seems enhanced with a lower molar mass of the linear unmodified PP.

Table 15: Molecular parameters from HT-SEC measurements

Sample	M_w [kg mol^{-1}]	M_n [kg mol^{-1}]	M_w/M_n	B_n
PP1B	611	317	1.92	0.08
PP2B	436	196	2.22	0.13
PP3B	333	151	2.20	0.25
PP4B	264	106	2.49	0.27

According to the reaction-scheme of LCB with PODIC in Figure 27, PP1 – with high molar mass – forms larger chain fragments with reduced ability for recombination during LCB. Furthermore it seems obvious, that chain mobility is detained by a higher number of entanglements in a melt of PP with higher molar mass, which is also in accordance to [33].

4.5. Influence of the extruder setup on LCB of PP *(Scale up; unpublished results)*

The Haake MiniLab II is a very reliable device for small-scale laboratory experiments. However, it is impossible to employ scale-up calculations for the given extruder setup, because the extrusion process is discontinuous. The melt is kneaded in a closed circle until it is ejected, which is necessary to reach the dwell time for total decomposition of the peroxide at 180°C. Higher temperatures, which would reduce decomposition time, are not favoured because of a higher β-scission rate. Such experimental setup is very uncommon in plastic manufacturing and therefore not comparable to industrial processes. It is obvious that scale-up makes sense with a different setup. Therefore, a change to a laboratory single screw extruder (compounder) and adjustment of the reaction parameters of the melt modification were done. Additionally, the single screw extruder offered the possibility to use different temperatures during processing. After some experiments, 170°C was chosen in the feeding zone for long chain branching with styrene and Peroxan HX (slightly above melting temperature to prevent clogging of the hopper) and 200°C in the middle zone and in the extruder dye. As number of revolutions per minute 50 rpm was chosen to ensure a dwell time of 1.5 min in the extruder, which is necessary for a total decomposition of the peroxide at 200°C. In case of LCB with PODIC it was not necessary to change the parameters, because of the low decomposition temperature of di-myristylperoxydicarbonate. Therefore, 170°C in the feeding zone, 180°C in the middle and 180°C in the dye at 100 rpm were chosen as processing parameters. Figure 64 shows the dynamic viscosity measurement of the up-scaled, the laboratory and the virgin grade PP. The modification in the single screw extruder gives higher values of the zero shear viscosity and the modulus crossover point indicates no significant changes in M_w, but broadening of MMD. Obviously, the polymer suffers less degradation in the single screw extruder compared to the twin-screw extruder.

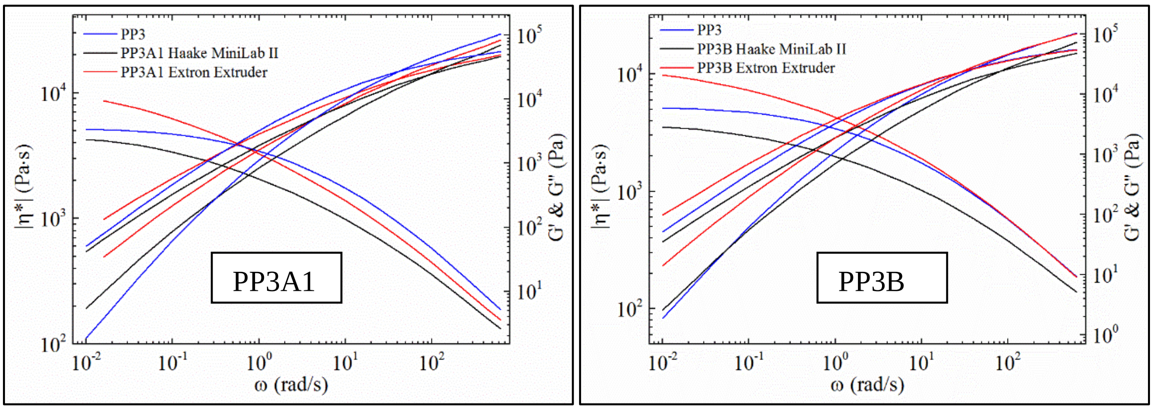

Figure 64: Comparison of the dynamic viscosity and moduli of the unmodified polymer (blue line) the Haake Mini LabII (black) and the single screw extruder (red line)

From the higher zero shear viscosity, also a higher value for the start-up curve in uniaxial elongational flow can be expected, which will result in higher absolute values of the elongational viscosity, as can be seen in Figure 65. Interestingly, the changes of the molecular structure deriving from LCB are not strongly affected by the extruder types. SHR is comparable as well as the shape of the SER-curves.

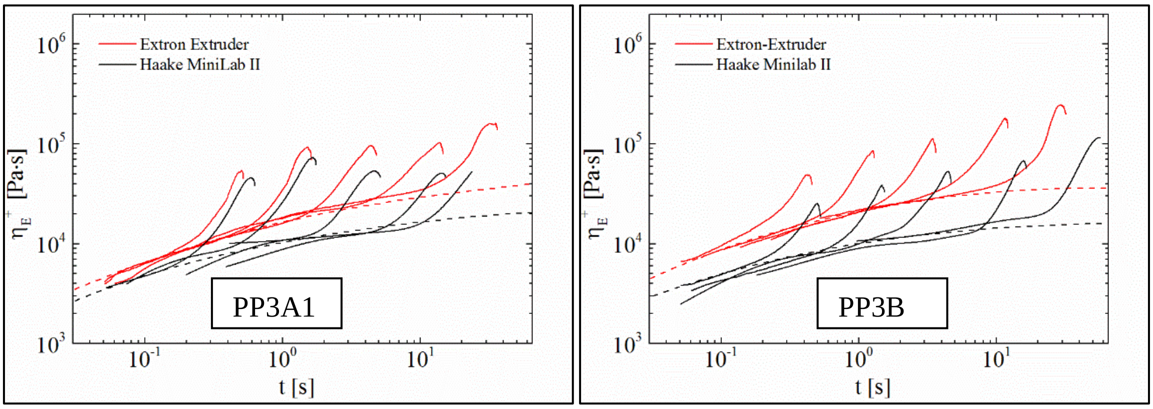

Figure 65: SER curves of the two different materials

After the successful optimisation of the melt modification using a single screw extruder, a computational scale-up reported by Maddock is possible [34] and will be part of future work.

4.6. Preparation of scCO2 blown PP foams *(unpublished)*

According to the procedure presented by Xu and co-workers [35], using the optimised conditions presented by Ding et al. [36], some preliminary foaming experiments were performed with supercritical CO_2 under high pressure in a 250 ml laboratory high pressure vessel (autoclave). The polymer samples were compression moulded to cylinders with 25 mm diameter and 10 mm height and approximately 4 g. The polymer and solid CO_2 were put in the autoclave, were charged with additional 55 bar CO_2 from a gas bottle and heated up to 170°C. The pressure was continuously regulated during the heating procedure. The polymer was saturated with CO_2 at 110 bar for 60 min and then cooled down to about 145°C. Then the pressure was released within 10 s and the steel jacket of the autoclave was cooled with water. For further information about the foaming procedure see [37].

Foaming of partially crystalline thermoplasts is a very challenging topic [38]. As expected, samples with low viscosity, like the linear injection moulding type PP4 cannot develop a foamed structure (Figure 66). The cells coagulated during expansion of the gas because of the low viscosity. The introduction of LCB did not change this. Obviously, the increase of the melt strength was not high enough for foam application. Hence PP4A1 and PP4A2 are not suitable for this procedure.

Figure 66: PP4 after foaming treatment in autoclave

Also, the linear extrusion type PP1 is not able to build a compact open cell foamed structure, although it has a significantly higher viscosity (Figure 67).

Figure 67: PP1 after foaming treatment in autoclave

For reasons of comparison, the industrial foaming grade HMS-PP (WB140HMS; long chain branched with butadiene and high temperature peroxides) was foamed via the aforementioned procedure as well, which gave a very good result. (Figure 68).

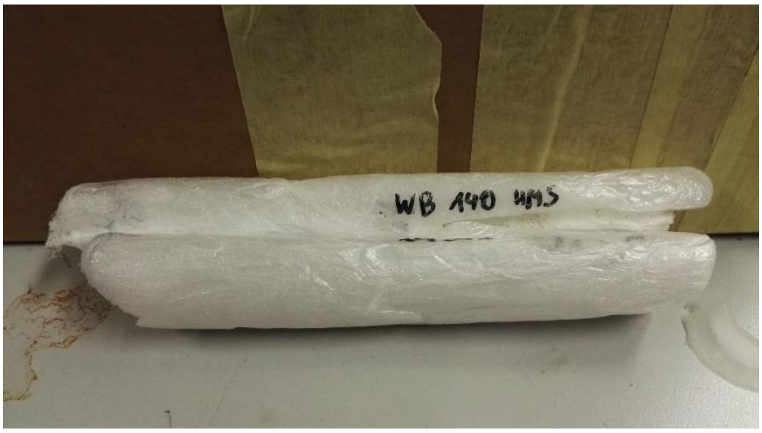

Figure 68: Foamed WB 140HMS

The LCB procedure with PODIC in combination with the extrusion grade PP1 (which has the highest M_w of the used feedstock materials) improves the formation of cells and enables the development of a foamed structure (Figure 69). The cell size distribution becomes more homogeneous.

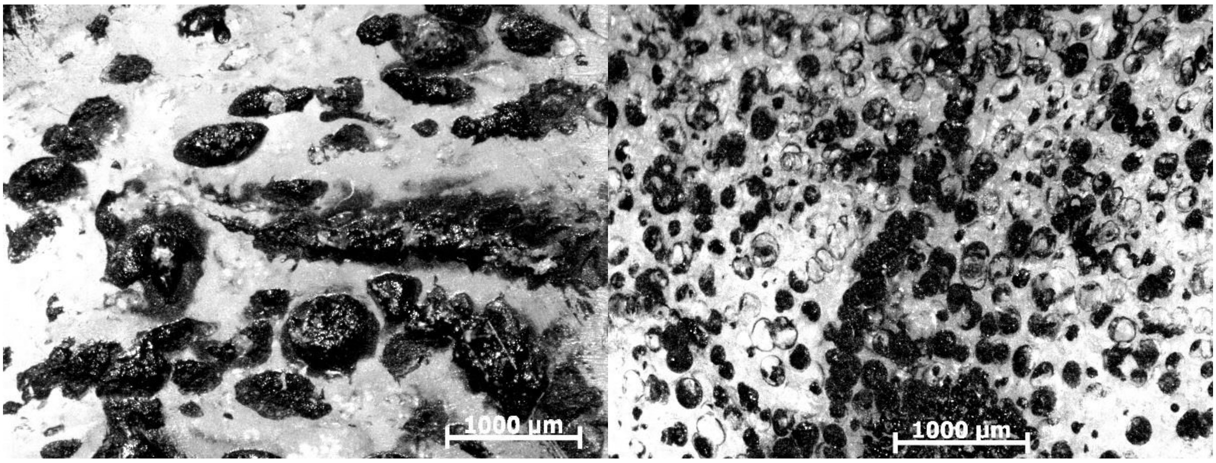

Figure 69: Comparison of foamed PP1 (left) and PP1B (right) after colouring of the cell-holes with ink

Very good results were obtained by long chain branching with styrene and peroxide (PP1A2). It was possible to increase the expansion ratio significantly and get a cell structure similar to WB140 HMS (Figure 70).

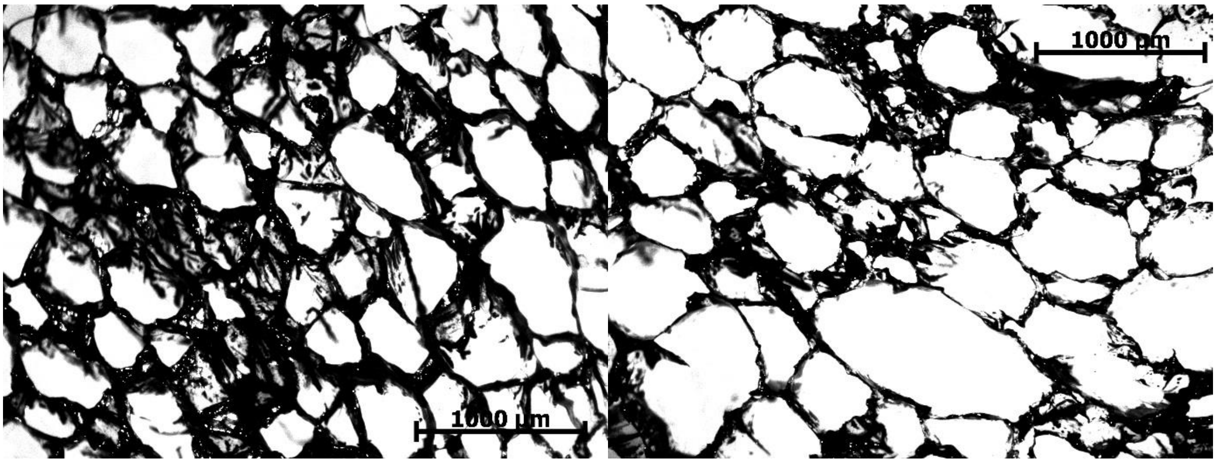

Figure 70: Comparison of foamed PP1A2 (left) and HMS-PP (right) after colouring of the cell-walls with ink

The melt strength of PP can be increased by increasing the molar mass (and therefore the zero shear viscosity) and by long chain branching (and therefore the strain hardening). Compared to the commercial HMS-PP, PP1A2 has a higher zero shear viscosity, but less strain hardening. The HMS-PP has a SHR higher than 100 (Figure

71). Within this study it was only possible to prepare a foam of high quality with a high molar mass grade PP as precursor. Further experiments also showed, that the commercial foaming PP-type allows a bigger processing window and gives comparable results. On the other hand, PP1A2 needed further optimisation and showed good results only under optimum parameters. A further optimisation of the branching procedure (more PODIC and more styrene and peroxide) will be necessary to obtain strain hardening comparable to the industrial foaming PP.

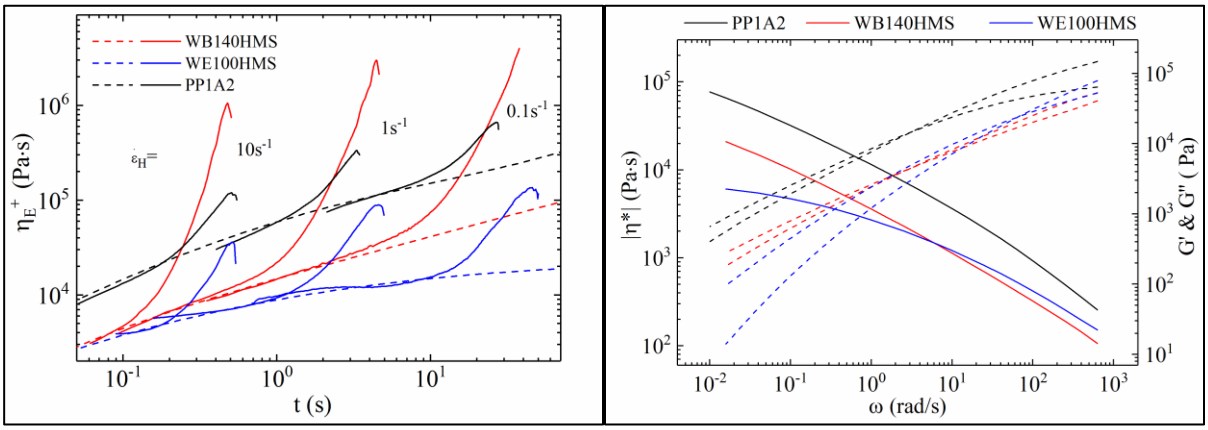

Figure 71: Comparison of the extensional (left) and the dynamic rheology (right) of PP1A2 and the two industrial HMS-PP

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4.8. Supplementary information

Sample name	Tm [°C]	Tc [°C]	Tg [°C]	ΔHm [J/g]	*E* [MPa]	ε [%]	a_{tN} [kJ/m^2]	Mw [kg/mol]	Mn [kg/mol]	η(ω=0.01) [Pa·s]
PP1	162.5	117.8	2.3	92.1	2219 ± 122	374 ± 83	43.6 ± 4.7	559	321	51200
PP1A1	161.7	131.2	4.0	93.6	1878 ± 200	654 ± 68	35.4 ± 3.4			50000
PP1A2	160.4	131.0	5.6	86.6	1683 ± 207	595 ± 62	24 ± 12.7			77300
PP1B	163.2	130.0	4.4	96.4	1616 ± 74	661 ± 51	45.7 ± 4.1			87700
extr. PP1B	164.0	127.6	---	97.8	---	---		611	317	61600
PP2	163.4	121.2	2.3	88.3	2358 ± 72	466 ± 58	39.6 ± 5.9	394	198	16200
PP2A1	161.7	128.6	3.4	87.9	2175 ± 64	44 ± 6	27.6 ± 3.8			16200
PP2A2	160.8	130.4	3.6	87.8	2207 ± 70	40 ± 6	24.6 ± 7.3			31600
PP2B	164.4	128.8	1.0	97.0	1800 ± 35	646 ± 37	42.4 ± 5.2			27100
extr. PP2B	163.5	128.3	---	98.0	---	---	---	436	196	18400
PP3	160.9	117.1	3.7	93.0	2075 ± 75	914 ± 37	23.9 ± 3.9	300	151	5100
PP3A1	159.5	127.1	3.4	88.1	1908 ± 158	776 ± 56	16.2 ± 2.8			4240
PP3A2	158.8	131.0	4.4	87.6	1970 ± 107	612 ± 32	12.3 ± 2.1			8620
PP3B	162.2	128.7	-3.0	96.6	1608 ± 83	973 ± 20	17.4 ± 2.8			3530
extr. PP3B	162.5	128.2	---	99.2	---		---	333	151	7510

PP4	162.8	115.9	1.7	91.5	1621 ± 183	684 ± 70	19.9 ± 6.4	227	99	2160
PP4A1	161.2	122.3	3.8	92.5	1880 ± 73	809 ± 62	15.1 ± 4.3			2360
PP4A2	161.8	127.4	4.5	93.6	2002 ± 90	32 ± 12	13.3 ± 0.8			10500
PP4B	163.7	123.6	-2.0	95.2	1505 ± 91	874 ± 117	21.4 ± 3.6			2400
extr. PP4B	163.2	127.1	---	100.5	---	---	---	264	106	2540
mBlend	130.5//160.5	118.7	2.0	21.3//82.8	2172 ± 115	986 ± 106	13.9 ± 1.7			5970
mBlendA1	128.2//160.5	118.0	4.0	17.6//85.1	1718 ± 68	914 ± 78	13.0 ± 1.3			4540
mBlendA2	126.7//159.0	118.7//126.44	6.0	14.9//81.1	1765 ± 80	619 ± 56	12.2 ± 1.5			12400
mBlendB	130.1//162.5	117.7//128.44	-3.0	21.9//86.1	1370 ± 74	709 ± 74	27.5 ± 4.3			5020
rPP	164.4	129.7	2.2	94.1	2021 ± 75	791 ± 37	37.1 ± 3.5			7920
rPPA1	160.2	130.8	3.8	97.5	1752 ± 52	711 ± 34	17.3 ± 5.4			8060
rPPA2	158.6	131.0	4.4	84.0	1830 ± 74	592 ± 25	11.7 ± 2.2			13900
rPPB	162.5	130.5	-.18	95.0	1661 ± 67	874 ± 88	32.0 ± 4			5430
rBlend	129.7//163.3	119.2//128.8	-2.2	19.9//91.3	1810 ± 87	36 ± 16	14.8 ± 1.9			1160
rBlendA1	126.9//159.1	117.2//127.0	-0.3	15.7//86.1	1580 ± 48	20 ± 2	13.7 ± 2.5			1030
rBlendA2	125.3//157.8	116.0//128.3	-3.4	10.7//83.7	1640 ± 35	17 ± 3	12.8 ± 1.4			2730
rBlendB	127.9//161.3	118.3//128.6	-9.2	14.4//93.6	1360 ± 82	23 ± 2	13.8 ± 2.2			1920

5. Conclusion and Summarised findings

Long chain branching (LCB) was presented as an innovative strategy for the treatment of polypropylene (PP) post-consumer waste. The key point was the significant improvement of the melt properties by means of strain hardening behaviour and an increase of the melt strength. Literature offers numerous possibilities to generate LCB in linear PP. Two methods were chosen:

- Peroxide (Peroxan HX; 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane) initiated grafting and branching with styrene, a mono-functional monomer
- Dimyristylperoxydicarbonate (PODIC) assisted LCB

PP-post-consumer waste – a commingled feedstock – offers some challenges that have to be considered:

- Impurities with high molar mass (polymers)
- Impurities with low molar mass (additives)
- Inorganic impurities from municipal household waste (metal, paper, etc.)

Inorganic impurities are expected without any influence on a radical induced modification of the polymer in melt. Within the project, only the influence of high molar mass impurities and low molar mass impurities have been studied.

High molar mass impurities were subdivided into two groups:

- Homogenous (different PP types)
- Heterogeneous (other polymers)

The most probable foreign polymer in PP post-consumer waste is polyethylene, because of the very similar density of the two polymers. Polyethylene with high density (PE-HD) was of special interest, because of the overlapping applications. Due to their poor miscibility, the dispersed phase separates from the matrix and forms dispersed droplets in the matrix. The size of the dispersed droplets depends on the interfacial tension between matrix (PP) and dispersed polymer, and on the viscosity of the two (or more) polymers. The resulting phase morphology affects primarily the mechanical properties, especially fracture behaviour.

The major findings were:

- In a system were matrix and dispersed phase have similar viscosities at the processing parameters the elongation at break is not affected by 10% PE-HD in PP-model mixtures. (*Paper I*)
- In a recycled system were matrix PP and dispersed PE-HD differ more remarkably in their viscosities, elongation at break is dramatically reduced (*Paper II*)

The radical induced structural changes vary strongly between PP and PE-HD. While PP undergoes chain scission, PE-HD undergoes branching and cross-linking. Co-agents for LCB of PP shall reduce chain scission, so they are expected to act equally for PE-HD and reduce cross-linking.

The major findings were:

- LCB of PP using a PODIC leads to the formation of xylene insoluble gel when PE-HD is present in the system. (*Paper I and II*)
- LCB of PP using styrene and peroxide also forms xylene insoluble gel. If the content of styrene monomer is increased, the xylene insoluble gel is reduced. (*Paper I and II*)
- Strain hardening was obtained for all modified samples and was comparable to the industrial film blowing grade HMS-PP WE100HMS. Strain hardening was not influenced negatively by the presence of PE-HD during LCB of PP at higher strain rates (*Paper I and II*)
- PODIC induced LCB improved the impact tensile strength in a PP/PE-blend with favourable viscosity ratio between matrix and dispersed phase (*Paper I*)
- In case of a PP/PE-blend with very high viscosity ratio between the blend components, LCB is not able to compensate the resulting negative effects from the phase morphology. Further negative side effects result from the cross-linking side reaction (*Paper II*)

As the recycled PP will always contain grades of different molar masses, it always will be a PP-blend. In this homogenous PP-blend, the melt viscosity depends on the composition of the different single PP-grades.

The major findings were:

- A high molar mass PP melt is characterised by a detained chain mobility due to a higher number of entanglements. Therefore the migration and recombination of chain fragments and long chain branching is less efficient, compared to a melt with low molar mass and high chain mobility (*Paper III*).
- Consequently, a high molar mass PP-grade (pipe extrusion) has a smaller average number of LCB per polymer chain compared to a low molar mass PP-type (injection moulding) under the same reaction conditions (*Paper III*).

Thus, two recycled post-consumer PP with similar MFI but different blend compositions (e.g. 50:50 blend of extrusion type PP with injection moulding PP and a 50:50 blend of casting and thermoforming PP) are expected to give different results in LCB (*part of future work*).

A further challenge is that the term “different PP-types” includes as well PP/PE random and block co-polymer. In literature, LCB of impact PP (PP/EPR-blend with 40-44% ethylene in EPR and 7% ethylene in total) has been studied by Chikhalikar et.al. Since a separate labelling of PP-co-polymers is not regulated by law, especially injection moulded food packaging made of PP-copolymers necessitates an intense discussion of LCB of reactor co-polymers (*part of future work*).

“Without additives, there are no plastics” – Polymer additives are an essential part in plastics industry. They ensure improved and tailor-made material properties and a long product life. Especially stabilisers are expected to influence a radical induced chemical modification of PP by scavenging the PP macroradical. This can reduce or improve the LCB efficiency. Furthermore the amount of required stabiliser can vary considerably between a long lifetime product (e.g. pipes, furniture, automotive parts,…) and short lifetime products or products with other special regulations (e.g. food packaging, consumables, baby toys,…).

The major findings were:

- The stabiliser effectiveness of the 4 virgin grade PP-samples was determined by thermal analysis of oxidation induction time (OIT). To exclude any interactions of the stabilisers during the LCB with PODIC, the stabilisers were removed by soxhlet-extraction (*Paper III*).

- The comparison of the viscosity curves of the extracted LCB-PP samples with the virgin LCB-PP samples showed remarkable differences in the absolute value of complex viscosity. For any further discussion not only the exact composition of the additive mixture, but also knowledge about interactions of the single stabilisers itself during reactive extrusion is necessary (*part of future work*).

The LCB reaction was repeated on a kg-scale extruder to investigate possible changes by scale-up and different extruder systems.

- The single screw extruder gave better results for the complex viscosity curves, the branching reaction seems to be not affected by the different extruder types, which was concluded from SER-measurement. All in all the reduced shear stress in a single screw extruder is favourable for the up-cycling of PP (*unpublished result*).
- Scale-up calculations are possible and will be part of future work.

Foaming of semi-crystalline polymers is a very challenging topic. Foam extrusion with chemical foaming agents or with expandable microspheres does not require such high melt strength like physical foaming.

- Foaming with supercritical CO_2 in an autoclave was successful using an extrusion type PP with high molar mass, which was treated with styrene and peroxide. After modification, the melt strength was high enough to generate a foamed structure with a narrow cell size distribution. However, strain hardening ratio of the industrial foaming type PP exceeds the values of the in house produced LCB-PP (*unpublished results*).
- After an adaption of the foaming parameters for the LCB-extrusion type PP1A2 the expansion ratio was approximately similar to the foamed industrial LCB-PP WB140HMS.

Outlook and suggestions

1. The LCB procedure using the PODIC is most promising and a simple implementation in a recycling process is expected.

2. The PODIC offers also the possibility for an impact modification in PP/PE-blends when the PP and the PE have similar viscosities.
3. The possible application (foam or blown film) depends on the MFI (molar mass) of the feedstock material. Beverage cups represent a homogenous fraction and can be used for blown films. Recycled pipes can offer the possibility to produce foams.
4. The combination of a creep test, a frequency sweep and SER measurements together with tensile and impact tensile tests is a good package to establish a quality management.

Upcycling of Polypropylene—The Influence of Polyethylene Impurities

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Long chain branching (LCB)—a well-known industrial process—is shown as an innovative tool for the treatment of PP post-consumer waste. The introduction of LCB by reactive extrusion does not only compensate the degradation during product life (e.g., thermally and UV-induced chain scission), it also improves the melt properties (e.g., melt strength, strain hardening). Thus, not only a recycling process, even a real "up-cycling" can be achieved. Compared with virgin material, PP from post-consumer waste contains impurities like other polyolefines (PE-HD, PE-LD, PE-LLD, copolymers), the total removal is economically not viable. Hence, the focus of this work was the influence of PE-HD on the LCB formation of PP. Based on model mixtures with virgin PP and 10% PE-HD, it is shown that PE-HD influences the mechanical properties and gel content of the chemically modified blend but has no detrimental effect on the improved melt properties. POLYM. ENG. SCI., 00:000–000, 2017. © 2017 Society of Plastics Engineers

INTRODUCTION

About 25.8 million tons of plastic post-consumer waste ended up in plastic waste upstream in 2014 (these are about 54% of the total plastic demand of EU27 + CH + NO). About 30.8% went to landfill, 39.5% were burnt and just 29.7% have been recycled [1]. After use, materials are still of value so burying them in a landfill or burning them is an egregious waste of resources. Recycling should be the preferred option for plastic waste, but in most cases energy recovery is the only alternative for a sustainable waste treatment. For the issue to give polymers a second life, research from a new perspective is necessary.

Recycling has to be separated in three different groups. The so-called primary recycling is the re-introduction of single-polymer waste material to the extrusion cycle to manufacture products of the same quality. Nowadays it mainly takes place in internal waste management of plastic processors. In most cases mechanical recycling or secondary recycling is the process to recover plastic waste for the re-use in manufacturing plastic products by mechanical means. Mechanical recycling can only be performed with single-polymer plastic. Separation, sorting, and washing are essential steps to produce a product of high quality. Chemical or tertiary recycling is a collective term for advanced processes to depolymerize plastic waste to recover base chemicals for the chemical industry [2, 3].

Polypropylene (PP), a widely used plastic for packaging and automotive applications, is a material that undergoes recycling-induced degradation, which makes it difficult to get a high quality product [4]. Especially shear induced chain scission during re-extrusion in mechanical recycling reduces viscosity and molar mass [5]. As a result, most of recycled PP is a product of worse quality, compared with virgin material, thus this process can be regarded as "down-cycling." Only a few concepts like the recovery of PP from car battery cases [6] or the blending of PP with Ethylene-Propylene-Rubber (EPR) as compatibilizer [7, 8] exist, which give satisfying material properties comparable to virgin material. However, its attractive property profile and remarkable growth rates over the last years and legislative pressure make it necessary to considerate innovative recycling concepts for PP.

Long chain branching (LCB) of PP for example can turn out as an innovative concept to give PP post-consumer waste a second life with improved material properties, especially considering its melt rheology [9–11]. LCB causes strain hardening and improves the melt strength of the PP. Its molar mass increases and its molar mass distribution (MMD) broadens in the reactive modification process. Special product applications, such as PP-foams, thereby become possible. The property profile of the PP will be extended in a way so that one can speak of a real "up-cycling."

LCB can be introduced by radical reactions in solid state, for example by electron beam irradiation [12] or grafting in presence of a peroxide and mono- or polyfunctional monomers [13, 14], or in melt by reactive extrusion and various co-reagents [15–18]. Co-reagents are necessary in melt to stabilize the PP-macroradical to prevent β-scission initiated degradation of the PP [19]. The stabilization of the macroradical is the most crucial point in LCB of PP. Reactive extrusion seems to be the most suitable method to establish a mechanical up-cycling, which includes a structural modification, to create LCB in PP post-consumer waste.

While extensive studies have been carried out on the LCB of virgin or reactor grade PP, only a few reports are available on the melt modification of post-consumer waste. Hettema et al. used similar concepts of melt modification with peroxide and mono- or polyfunctional monomers to improve the mechanical properties (e.g., impact strength) of PE from recycled bottle waste. This recycled bottle waste contained 10% of PP as impurity [20]. In general, the challenges in chemical modification of polyolefin post-consumer waste can be summed up in four groups: high molecular impurities like other plastics (in case of PP especially PE), low molecular impurities like stabilizers, homo molecular impurities like PPs with different molar masses, or co-polymers, and inorganic impurities like fillers or metal [21].

According to Lagendijk et al. and Wong et al., peroxydicarbonates (PODIC), a special class of peroxides [17], or styrene in combination with peroxide [22], can be used to create LCB in

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melt. Lagendijk et al. showed a good LCB-efficiency with PODIC that have long alipathic chains. Stabilization of the macroradical and recombination of polymer chains are mediated by the peroxide itself. An exact mechanism is still not proposed. Wong et al. described the melt rheology of styrene grafted PP. They showed that recombination of styrene grafted PP-chains occurs, when a certain amount of styrene and peroxide was used. First long chain branches are generated, this turns into cross-linking if higher amounts of styrene and peroxide are used. Similar processes, that use the combination of a mono- or polyfunctional monomer with a peroxide are widely discussed in literature [18, 23], and have been successfully used in industry [24]. But the use of polyfunctional monomers, that can form xylene insoluble particles by homopolymerization, makes it difficult to discuss a possible gel content properly.

In this study both approaches were used, and also the influence of PE-HD as a high molecular impurity in PP post-consumer waste was studied with model mixtures. About 10% PE-HD were chosen as the lowest amount of impurity a real system will contain [4].

EXPERIMENTAL SECTION

Materials

Isotactic PP homopolymer (HD601CF) and PE-HD (CG9620) for the model mixtures were provided by Borealis Polyolefines. Styrene (≥99%, Aldrich) was used without further purification. The peroxide Peroxan HX (2,5-Dimethyl-2,5-di-(tert.-butylperoxy)-hexane; 10 h half life time at 115°C) and the PODIC Peroxan C126 (Di-tetradecylperoxydicarbonate; 10 h half life time at 48°C) were supplied by Pergan. Irganox 1010 [Pentaerythritol tetrakis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)], a phenolic heat stabilizer, was supplied by BASF.

Sample Preparation

Virgin PP and PE-HD were shredded with a Fritsch granulator "Pulverisette 16" to produce particles with a mean diameter of 1 mm. Styrene and peroxide were premixed and dropped on the polymer particles and subsequently stored overnight at room temperature to allow monomer and peroxide to diffuse into the particles [22, 25]. Two different concentrations of peroxide and styrene (A1 and A2) were chosen. PODIC was dissolved in 50 mL n-hexane and pured on the grinded polymer, mixed and then stored at room temperature until the solvent evaporated (B) [17]. Reactive extrusion was carried out in a Haake Mini Lab II conically shaped twin-screw extruder at 180°C and 100 rpm screw speed for 6 min. After 5 min, when the peroxides should be completely decomposed (estimated from half life time), 1 mg (about 0.02%) Irganox 1010 was added in order to prevent further degradation. Sample names and abbreviations are listed in Table 1. For the tensile tests and the impact tensile tests, specimens were injection molded with a Haake Mini Jet at 230°C melt- and 80°C mold temperature. For the rheology measurements compression molded plates were prepared at 180°C and 25 bar.

TABLE 1. Sample specifications.

Sample	Sample specification
PP1	PP, extruded and stabilized
PP1A1	20 mmol/kg peroxide, 480 mmol/kg styrene (5%)
PP1A2	35 mmol/kg peroxide, 840 mmol/kg styrene (9%)
PP1B	20 mmol/kg PODIC (1%)
PP1PE1	PP/PE-Blend (10% PE-HD), extruded and stabilized
PP1PE1A1	20 mmol/kg peroxide, 480 mmol/kg styrene (5%)
PP1PE1A2	35 mmol/kg peroxide, 840 mmol/kg styrene (9%)
PP1PE1B	20 mmol/kg PODIC (1%)

Thermal Analysis

Approximately 5 mg of the polymer sample were put in TA standard aluminum pans, sealed and measured on a TA Q2000 DSC. Samples were heated to 200°C with 10 K/min to eliminate the thermal history, then cooled down to room temperature (10 K/min) and heated up again to 200°C (10 K/min). TA Universal analysis software was used to determine melting- (T_m) and crystallization temperature (T_c), as well as the melting enthalpy (ΔH_m). Glass transition temperature (T_g) was determined on a TA 2980 DMA in 3-point-bending mode. Specimen, which were cut off from injection molded tensile test specimen, were stored at 80°C overnight to recrystallize the outer edges of the specimen. The sample was cooled down to −50°C and then heated up at 1 K/min to 50°C. T_g was determined with TA Universal analysis software using the peak maximum of the loss modulus. The content of volatiles was determined by TGA. Approximately 10 mg of the samples were heated up from room temperature to 600°C under nitrogen atmosphere. Temperature at 97% mass loss (T_{97}) was chosen as degradation temperature and mass loss at 300°C (m_{T300}) was used for the content of volatiles (decomposition products of peroxide, residual monomer, etc.).

Gel Content

About 300 mg of the polymer were weighed into paper filters and refluxed in 100 mL xylene for 24 h to determine the insoluble gel content.

Tensile Tests and Tensile Impact Strength

Tensile test specimens according to ISO 527-2 type 5A were injection molded. The test machine (Zwick 050) was equipped with an extensometer, the test speed was 10 mm/min. Impact tensile test specimens with 60 mm × 10 mm × 1 mm were injection molded under the same conditions. Samples were notched and tested according to ISO 8256 method A on an Instron CEAST 9050 impact pendulum (2 J hammer; cross head mass = 15 g). The fracture surfaces were characterized with a Scanning Electron Microscope (SEM) FEI Philips Model XL30. For SEM investigations a gold layer was previously sputtered on the samples.

Dynamic Rheology

Discs with 25 mm diameter and 1.2 mm thickness for dynamic rheology were compression molded. Dynamic rheology measurements were carried out on a Plate-Plate Anton Paar MCR 301 rheometer equipped with CTD 450 heating chamber under nitrogen at 180°C with 1 mm gap size. Frequency was chosen between 628 and 0.01 rad/s, deformation was raised from 1% to 2% logarithmically during the measurement.

Deformation was in the linear viscoelastic range, which was checked by amplitude sweep. Thermal stability over time was proven by a time sweep over 2 h at constant conditions. All samples satisfied the stability and measurement conditions for the frequency sweep.

Extensional Rheology

Stripes with 8 mm width for extensional rheology were cut from 100 mm × 100 mm × 0.5 mm sheets after compression molding at 180°C. Extensional rheology was measured using a Sentmanat Extensional Rheometer (SER-HPV 1) for Anton Paar rheometers, at 180°C and five different strain rates ($\dot{\varepsilon} = 10\ \mathrm{s}^{-1}$; $3\ \mathrm{s}^{-1}$; $1\ \mathrm{s}^{-1}$; $0.3\ \mathrm{s}^{-1}$; $0.1\ \mathrm{s}^{-1}$). Start-up curve was measured with a steady shear experiment at plate-plate system and two different shear rates ($0.001\ \mathrm{s}^{-1}$ and $0.1\ \mathrm{s}^{-1}$).

RESULTS AND DISCUSSION

Thermal Analysis

Table 2 shows all collected data from thermal analysis. Melting and decomposition temperature of PP-phase decreases by styrene modification and increases with PODIC. Figure 1 shows, for instance, the cooling and second heating curves of PP1PE1 and PP1PE1B. The depicted polymer blend shows one additional melting peak of the PE-phase, but only one crystallization peak. The curve of PP1PE1B shows that structural modification improves the crystallization ability of the PP-phase, which separates from the PE crystallization peak. Zhou et al. and Tian et al. explain the higher T_c of LCB-PP with the structure of the polymer itself that acts as nucleating agent [11, 26] and Tabatabei et al. connects it with residuals from the production process [27]. Furthermore the melting peak of the modified sample PP1PE1B becomes broader; ΔH_m increased at the same time slightly. PP1A1/PP1A2 as well as PP1PE1A1/PP1PE1A2 have lower ΔH_m and T_m than the unmodified sample. This decrease of ΔH_m and T_m with higher amount of grafted monomer is in accordance to literature [8].

As expected, the content of volatiles increases from 1% to 1.4% (PP1A1 to PP1A2) and from 0.8% to 1.2% (PP1PE1A2 to PP1PE1A2). If virtually no volatiles get lost during extrusion, about 0.6% (A1) of volatiles and 1% (A2), respectively, can be assigned to the decomposition products of the peroxide (e.g., tert-butanol), the difference to $m_{\mathrm{T}300}$ is attributed to the residual monomer. Addition of PE-HD reduces the residual content of volatiles by 0.2%. Borsig et al. also observed the higher reactivity and explained it by a better solubility of the co-agents in the PE-phase [28]. In case of PODIC modified sample, a volatile content of 0.6% for PP1B and 0.5% for PP1PE1B was obtained. About 1% of PODIC was added, but long aliphatic chains have lower volatility and higher temperature resistance compared with the small decomposition products from Peroxan HX.

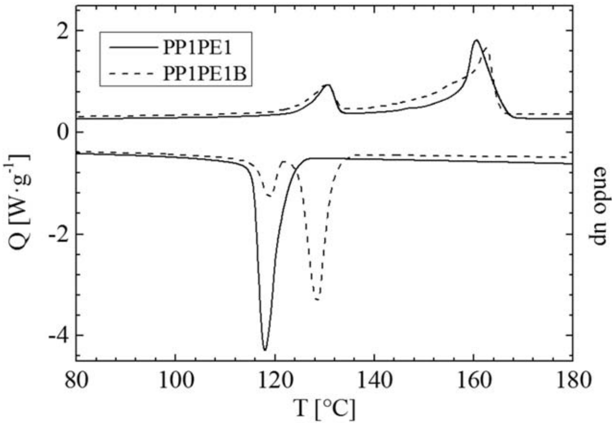


FIG. 1. DSC scan of PP1PE1 and PP1PE1B.

T_g decreases below 0°C in PP1B and PP1PE1B with PODIC as co-reagent; therefore we suggest that long-chain aliphatic residuals act as softening agent. Addition of PE-HD reduces T_g in PP1PE1 for about 1.7°C compared with PP1. Modification with styrene and peroxide does not influence T_g a lot in pure PP samples (PP1A1 and PP1A2). However, T_g of polymer blends increases from 2°C (PP1PE1) to 4°C (PP1PE1A1) and 6°C (PP1PE1A2), respectively.

Gel Content

Figure 2 shows that even in unblended PP1A2 and PP1B, chemical modification can form a small amount of highly branched gel particles. As expected, the presence of PE-HD increases this amount in the case of PP1PE1A1 and PP1PE1B threefold. Interestingly, a higher amount of styrene and peroxide reduces the gel content again, which can be seen for PP1PE1A2. A reduction of cross-linking side reactions in PE-phase can thus be considered.

Mechanical properties of resulted samples are directly influenced by the chemical (grafting) and structural modification (LCB). Figure 3 shows the tensile modulus of unmodified PP1, exhibiting a slight increase by the addition of 10% PE-HD (PP1PE1) and a slight increase of the elongation at break, which is in accordance to literature [8, 29]. PP1A1 and PP1A2 as well as PP1PE1A1 and PP1PE1A2 show that modification with

TABLE 2. Summary of thermal analysis of model mixtures.

Sample	T_m [°C]	T_c [°C]	ΔH_m [J/g]	T_g [°C]	$T_{97\%}$ [°C]	$m_{\mathrm{T}(300)}$ [%]
PP1	160.9	117.1	93.0	3.7	344.9	100.0
PP1A1	159.5	127.1	88.1	3.4	332.3	99.0
PP1A2	158.8	131.0	87.6	4.4	324.1	98.6
PP1B	162.2	128.7	96.6	−3.0	347.9	99.4
PP1PE1	130.5//160.5	118.7	21.3//82.8	2.0	366.7	100.0
PP1PE1A1	128.2//160.5	118.0	17.6//85.1	4.0	342.7	99.2
PP1PE1A2	126.7//159.0	118.7//126.44	14.9//81.1	6.0	332.5	98.8
PP1PE1B	130.1//162.5	117.7//128.4	21.9//86.1	−3.0	367.9	99.5

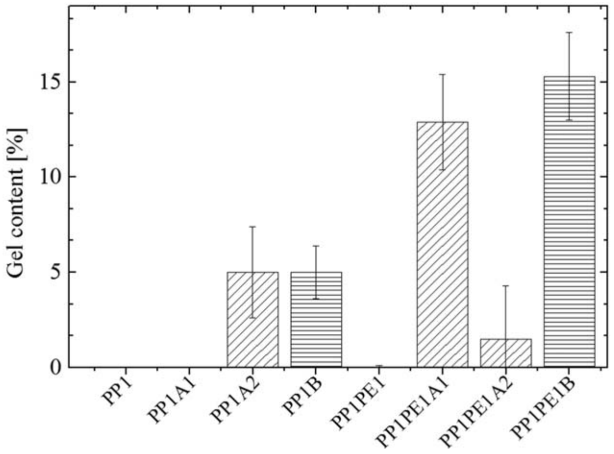


FIG. 2. Gel content of the model mixtures.

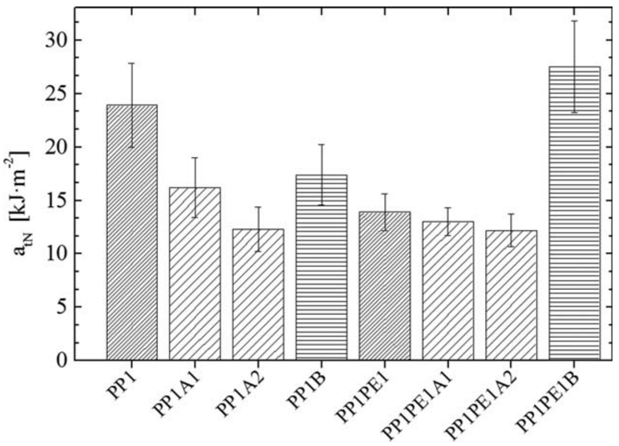


FIG. 5. Impact tensile strength of the model mixtures.

styrene reduces the tensile modulus at first and increases it again with a higher amount of styrene and peroxide. Elongation at break (Fig. 4) decreases from PP1A1 to PP1A2 due to higher amounts of styrene. The same trend occurs for PP1PE1A1 and PP1PE1A2, but elongation of PP1PE1A1 is 30% higher than for PP1A1 and has nearly the same value as PP1, despite the high gel content of more than 10%. However, higher amounts of styrene reduce elongation at break by one third, compared with the unmodified material, a higher influence on the mechanical properties of the grafting monomer has to be considered [30].

PODIC reduces the tensile modulus (PP1B and PP1PE1B), although the degree of crystallinity increases (higher ΔH_m in Table 2). The formation of LCB and long-chain aliphatic

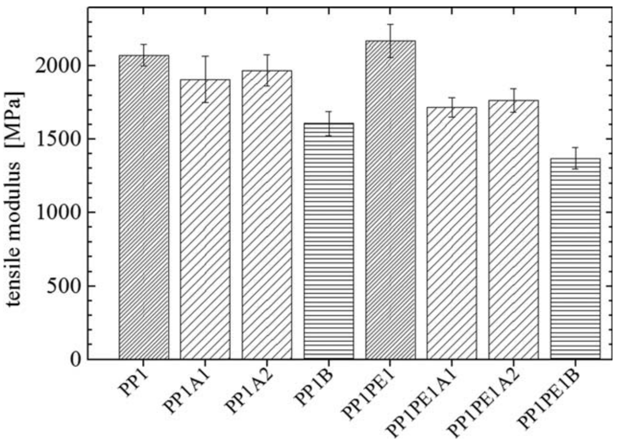


FIG. 3. Tensile moduli of the model mixtures.

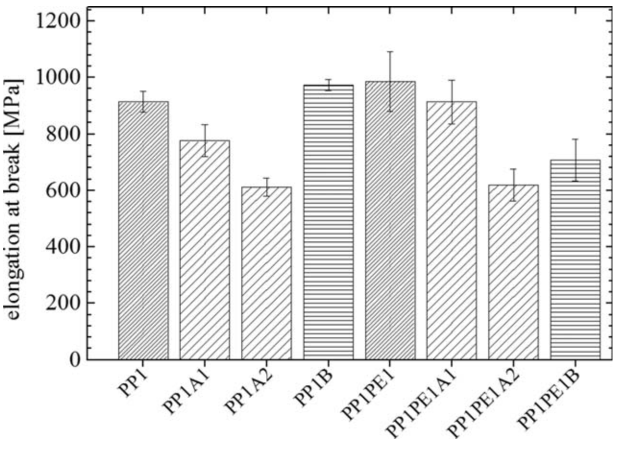


FIG. 4. Elongation at break of the model mixtures.

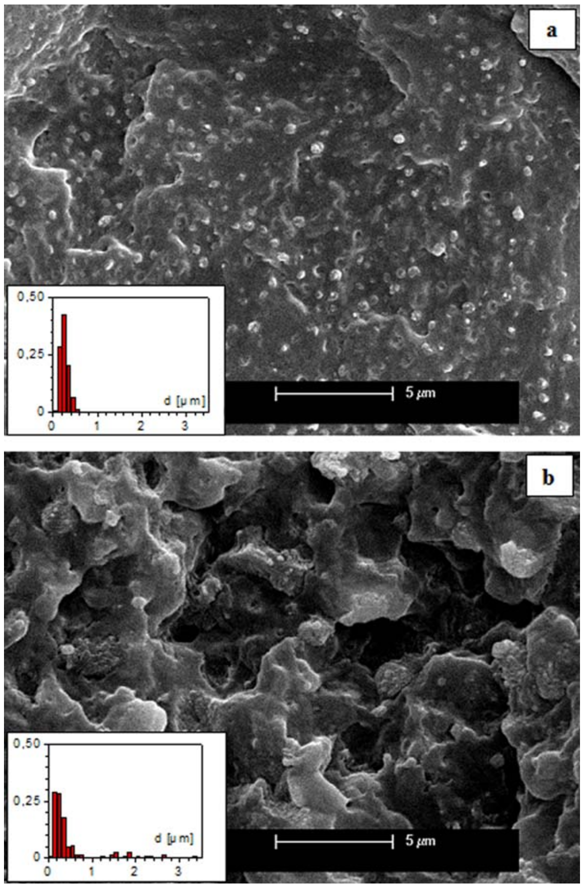


FIG. 6. Fracture surfaces of tensile impacted samples and particle size distribution; (a)PP1PE1; (b) PP1PE1B. [Color figure can be viewed at wileyonlinelibrary.com]

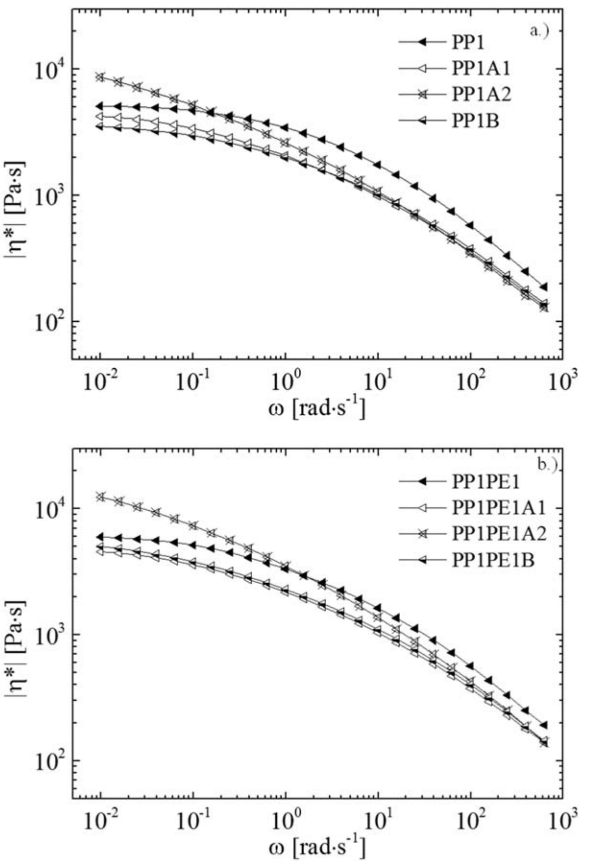


FIG. 7. (a) Complex viscosity curves of the PP-samples. (b) Complex viscosity of the PP7PE-blends.

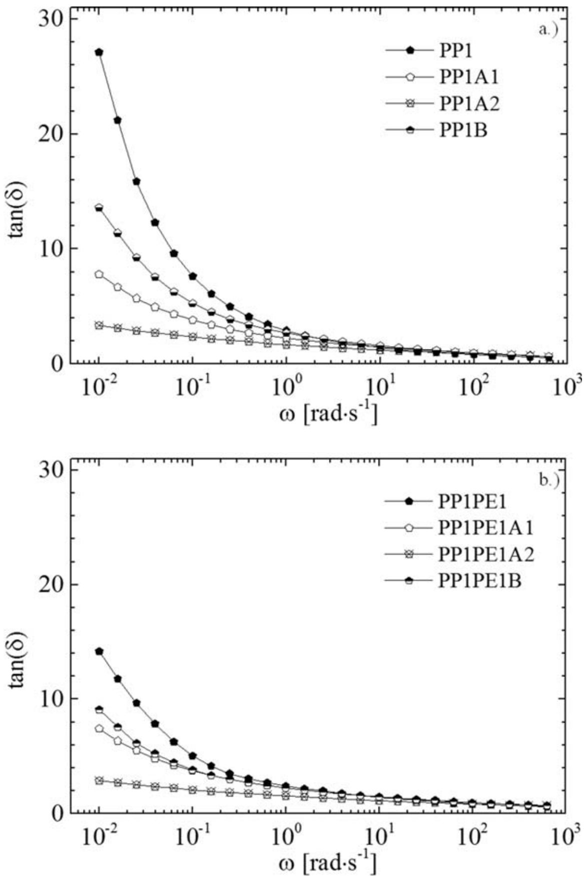


FIG. 8. Loss factor of the (a) PP-samples; (b) PP/PE-blends.

decomposition products from the peroxide, and a lower T_g are possible explanations. The same reasons hold valid for the higher elongation at break of PP1B. However, PP1PE1B has a significant lower elongation at break (about 30%). Although a significant amount of xylene insoluble gel in case of PP1PE1A1 and PP1PE1B was formed, elongation at break was only reduced for PP1PE1B. As shown by Braun et al., side reactions of PE-HD with peroxide can form highly branched gel particles that reduce elongation at break [31]. The formation of microgels was also described by Chikhalikar et al., when they used PODIC for the LCB of PP impact copolymer [32].

The results of tensile impact tests are shown in Fig. 5. Interestingly, the impact tensile strength of PP1PE1B increased to 27 kJ/m^2, which is almost twice the value of PP1PE1 and 10% more than unmodified PP1. Chodak et al., showed that peroxide initiated cross-linking of PP/LDPE-blends in presence of hydroquinone increases impact strength and gel content. The quinone delays the cross-linking in LDPE and activates cross-linking in PP [33]. It is supposed that PODIC acts in a similar way. However, PP1PE1A1 does not show an increase in impact tensile strength, despite of a similar gel content compared with PP1PE1B. PP1A2 and PP1PE1A2 have nearly the same impact tensile strength.

Looking at the fracture surfaces of the impact tested specimens (Fig. 6) some differences can be observed. In PP1PE1 the PE-HD is finely dispersed with an average particle diameter of 0.26 μm. The holes are a result of the typical pull out of particles which can be found at the opposite fracture surface. The appearance of the fracture is flat, no "typical" features of micromechanical effects of toughening, that is, voiding and/or fibrillation, are visible. The PODIC treated PP1PE1B shows a considerable bumpy surface. In addition to the small particles a second species of bigger particles between 1.2 and 3.4 μm diameter are visible. The bigger particles are often cut through reflecting a good phase adhesion. The structure of these particles appears often like a combination of cross-linked material and aggregated small particles.

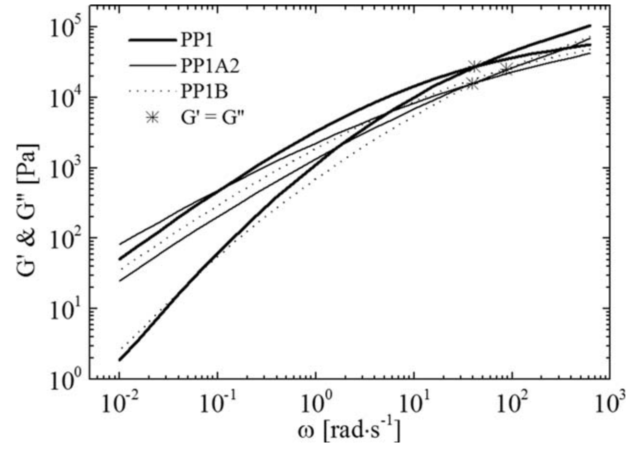


FIG. 9. Comparison of the storage and loss modulus of unmodified and modified PP-samples.

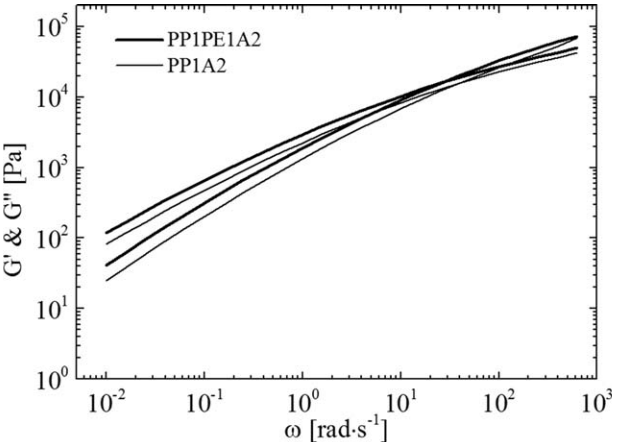


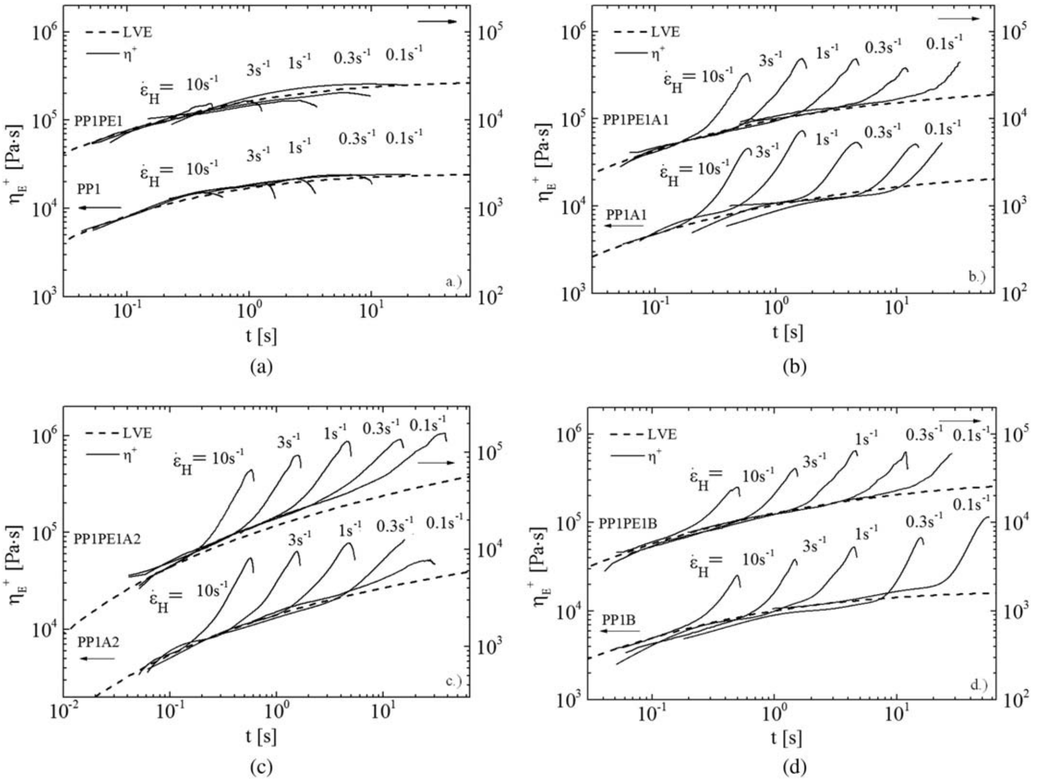
FIG. 10. Influence of 10% PE-HD on the modulus curves after modification A2.

Rheology

According to literature, melt rheology is not only influenced by the molecular structure, but also by the phase structure [34, 35]. The rheology data (obtained at 180°C) for the pure PP samples are shown in Fig. 7a. Linear unmodified PP1 reaches the zero shear viscosity plateau (η^0) already at $\omega > 0.01$ rad/s. This can also be seen by the strong increase of the loss factor [tan(δ)] in Fig. 8a. Styrene modified samples PP1A1 and PP1B show a broader transition from power law to the zero-shear viscosity regime. This transition becomes the broadest in case of PP1A2 as, compared with the other specimen, $|\eta^*|$ becomes highest in the low frequency area and pronounced shear thinning at high ω is shown. Viscosity and therefore molar mass increases by grafting of styrene onto the PP backbone, but also by recombination. A shift of the crossover point of storage and loss modulus can also serve as an indication about changes in the molar mass and the MMD [36]. Figure 9 shows the storage (G') and loss modulus (G'') of PP1, PP1A2, and PP1B. The crossover point ($G' = G''$) of PP1B shifts to higher ω (lower molar mass) but also to a lower crossover modulus (broader MMD). However, the crossover point of PP1A2 shifted to lower G (broader MMD) and lower ω (higher molar mass). The structural modified blends PP1PE1A1, PP1PE1A2, and PP1PE1B show similar changes of $|\eta^*|$ (Fig. 7b) and tan(δ) (Fig. 8b). This is highlighted in Fig. 10, where the moduli of PP1A2 and PP1PE1A2 are shown. As can be seen, both curves have a similar shape, the cross over point of PP1PE1A2 shifts to lower ω compared with PP1A2, which can be a hint for a higher molar mass. This is in agreement with the $|\eta^*|$ at $\omega = 0.01$ rad/s, which is significantly higher for PP1PE1A2 compared with PP1A2.- This is also the case for PP1PE1B compared with PP1B.

Summarizing the results from oscillatory experiments which are in good agreement with literature [36, 37], it is shown that chemical modification increases molar mass and broadens MMD. The formation of a branched structure id also suggested [34, 38]. For a better verification of LCB, extensional viscosity measurements were performed.

SER-measurements of polymer samples show that unmodified samples PP1 and PP1PE1 show no strain hardening (Fig.



(a) (b)

(c) (d)

FIG. 11. SER-measurements of (a) PP1 and PP1PE1; (b) PP1A1 and PP1PE1A1; (d) PP1A2 and PP1PE1A2; (d) PP1B and PP1PE1B.

11a). PP1A1 and PP1A2, show a deviation from linear viscoelastic (LVE) behavior (Fig. 11b,c). After modification method A1 and A2, the strain hardening index decreases with decreasing strain rate. The Hencky strain ε_H, where extensional viscosity $\eta_E{}^+$ starts to deviate from the threefold of the linear viscoelastic start-up curve, decreases from 1.4 (A1) to 1.0 (A2). The maximum strain remained constant at 5.0 for A1 and A2. The modification with PODIC (B) also introduced strain hardening to all samples (Fig. 11d), but no strain rate dependence of the strain hardening was found here. According to Gabriel et al. a pronounced strain hardening at higher strain rates can be a hint for a higher degree of LCB [39]. The samples that contain 10% PE-HD show nearly the same behavior of extensional viscosity; however, it is pointed out that a significant amount of gel was formed in PP1PE1A1 and PP1PE1B. We propose that PE-HD do not negatively influence the long chain branching reaction in the PP-phase and therefore the rheological improvement (especially strain hardening) of the chemically modified samples.

CONCLUSIONS

In the present work long chain branching (LCB) was used to up-cycle PP. Reactive extrusion with peroxide and monomer (modification A1 and A2) and peroxydicarbonates (PODIC; modification B) was chosen as the method. Model mixtures from pure PP and PP/PE-blends containing 10% of PE-HD were prepared to study the influence of PE-HD on the melt modification of PP.

Results from the pure PP samples show that PODIC do not only introduce strain hardening, they also improve the mechanical properties (higher elongation at break) and thermal properties (lower T_g and higher T_m, T_c, and ΔH_m). Modification with styrene and peroxide showed mixed results. It was possible to improve melt properties, but elongation at break and impact tensile strength worsened. Grafting with styrene reduced decomposition temperature and samples contained of up to 1.4% of volatile residuals.

When 10% of PE-HD were added to the system, the gel content increases, which has to be considered in manufacturing processes like film blowing and foaming. This influences the elongation at break, which increases with modification A1 (styrene and peroxide; 5% additives) and decreases with modification B (PODIC) compared with pure PP samples. However, elongation at break does not change for modification A2 (styrene and peroxide; 9%). Results from impact tensile test show a significant increase of impact tensile strength with modification B. Melting properties were not influenced by the addition of 10% PE-HD; however, thermal stability was improved and the content of volatile residuals of A1 and A2 was reduced.

Modification with PODIC turned out to be a suitable method to generate LCB in pure PP, but in the presence of PE-HD typical side reactions (branching and cross-linking of PE) take place, that influence the mechanical properties. This is also the case when modification A1 was used for the blend. But especially results from elongation at break and impact tensile strength suggest a difference in the side reactions that occur. However, when the amount of styrene and peroxide was increased in modification A2, the mechanical properties hardly change, when PE-HD was added, compared with the pure PP. Nevertheless, the drawback of nearly 20% impurities in PP1PE1A2 will be a limitation for possible applications. Further improvements will be part of future work.

Results from oscillatory rheology suggest a broadening of MMD for all modifications and an increase of molar mass for modification A2, regardless of the PE-HD. Strain hardening was proven by extensional rheology measurements. Strain hardening was also not influenced by the addition of 10% PE-HD, as well as by the gel content. With these results, the preparation of a PP-foam looks promising.

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Long chain branching as an innovative up-cycling process of polypropylene post-consumer waste – Possibilities and limitations

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ABSTRACT

Long chain branching (LCB) was used the first time as an innovative tool for value adding to PP from household post-consumer waste. Due to the highly improved melt properties, the possible application profile is extended and not only a "re-cycling" process, even a real "up-cycling" is presented. The used PP was collected from commingled household polyolefin waste, which contained different types of PP and macromolecular impurities such as 10% of polyethylene with high density (PE-HD). In addition, a single PP waste fraction from cleaned beverage and yoghurt cups was manually sorted. The up-cycled PP from single polymer waste, as well as the post-consumer blend, showed pronounced strain hardening and increased melt strength, which was comparable to LCB-PP prepared from virgin PP. However, the up-cycled post-consumer blend showed weaker mechanical performance especially low elongation at break due to PE-HD.

1. Introduction

Polypropylene (PP) with a share of 19.1% on European plastic demand in 2015 is the second most important polymer. Together with polyethylene (PE), these two polyolefins represent 48.5% of the European plastic demand. In case of PP, about one-half of the produced material is used for packaging and therefore for single use. So nearly half of the produced PP ends up after a short period of use as post-consumer waste. 25.8 million tons of plastic waste accrued in Europe in 2014, 30.8% went to landfill, 39.5% were incinerated for energy recovery and 29.7% were mechanically or chemically recycled. Despite increasing recycling rates, incineration or energy recovery still is the preferred option for the treatment of mixed municipal plastics waste especially in Europe (PlasticsEurope, 2016).

Because of the continuously changing composition of the material that has to be sorted, mechanical recycling of post-consumer PP has appeared to be a tough challenge (Cimpan et al., 2015). Most plastics are not miscible and the resulting phase separation influences Young's modulus and other mechanical properties negatively (Goodship, 2007). Several studies have shown that up to 10% of foreign material still remain in recycled PP after sorting by trained personnel (Brandrup, 1996). Sink-float with water as medium is a cost effective standard separation technology for commingled polymer waste. Polyolefin fractions containing PE and PP can be separated from plastics with a specific gravity higher than 1 g/cm^3 (like Polyvinylchloride and Polyethylene terephthalate). However, the polyolefin mixtures are not suitable for high quality products, for this, the content of the main component PP or PE respectively, should be higher than 97% (Bakker et al., 2009). Nonetheless, it is worth noting, that physical processing and sorting technologies have reached a high standard during the last decades (Serranti et al., 2015) which also allows a sorting of single polymer waste by colour (Safavi et al., 2010).

Furthermore, PP undergoes thermo-mechanical, thermo-oxidative and shear-induced degradation during product life and through mechanical recycling. This results in a decrease of the molar mass and a deterioration of the mechanical properties (Incarnato et al., 1999; da Costa et al., 2007), and therefore, results in an economic disadvantage of recycled PP compared to virgin material. The prices for recycling-grade PP granules fluctuate strongly, the average price over the first half year 2017 is about 0.78 ± 0.14 €/kg. Virgin grade PP granules compete with a price of 0.79 ± 0.05 €/kg at the same period (Plasticker, 2017). To improve the mechanical and thermal properties and therefore the competitiveness of recycled PP, additives such as mineral fillers and elastomers can be added (Brachet et al., 2008). Elastomers like ethylene-propylene-rubber (EPR) are also capable to compensate negative side effects of PP-blends with PE impurities (Teh et al.,

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1994). However, HMS-PP (high melt strength PP), a special PP-type for foaming and film blowing is currently traded with a price 0.50 €/kg higher compared to standard linear PP resins. That means that there is some space for modification from the economic point of view.

Long chain branching (LCB) is a well-known industrial post-reactor process to produce PP with high melt strength and strain hardening (HMS-PP). Furthermore, the molar mass is increased and the molar mass distribution is broadened (Gotsis et al., 2004). LCB is a combination of radical induced activation of PP, partial chain scission and recombination. At temperatures below the melting point of PP (solid phase reaction), recombination overwhelms chain scission. This reverses in melt, so the PP macroradical needs to be stabilized with special co-agents. A reaction scheme is given in Fig. 1.

Important studies on the mechanism of LCB formation are reported by (Rätzsch, 1999). Several methods are reported in literature, e.g. LCB-PP can be produced by electron beam irradiation in solid phase (Auhl et al., 2004) – Amppleo™ by Braskem –, by branching in melt with a monomer and peroxide (Zhang et al., 2013) – Daploy™ by Borealis – or by reactive extrusion with peroxydicarbonates (PODIC) with long aliphatic side chains (Lagendijk et al., 2001). Due to its higher melt strength and strain hardening, LCP-PP finds application in film blowing and foaming processes for which linear PP is not suitable (Stange and Münstedt, 2006; Stange et al., 2005).

In our previous work (Kamleitner et al., 2017) model mixtures from PP and PP containing 10% PE-HD as impurity (both from virgin film grade material; the viscosity ratio of dispersed PE in matrix PP ≈ 1:6 at 180 °C) were long chain branched according to (Wong and Baker, 1997) and (Lagendijk et al., 2001) respectively. Each modified sample showed strain hardening behaviour and mechanical properties increased significantly, despite the PE-HD impurities.

LCB offers the possibility to extend the application profile of recycled material to higher value applications like blow moulded films and foams and has high potential to become an innovative recycling process, which contains a value adding to PP. Consequently, if "down-cycling" is used for low value application of recycled material, one can speak of "up-cycling" in the case of LCB of PP post-consumer waste, which is emphasised in Fig. 2.

The results from our previous work shall be used to apply our "up-cycling"- concept on PP from post-consumer household waste and discuss challenges that occur from a recycled feedstock. Especially 10% impurities, a recycled system is likely to contain of, from different PE-HD packaging material and the resulting limitations will be one focus of our study. Dynamic and elongational rheology (the most convenient tools for LCB detection) will be used to discuss the changes of the molecular structure. Tensile and impact tensile tests shall complete the data set.

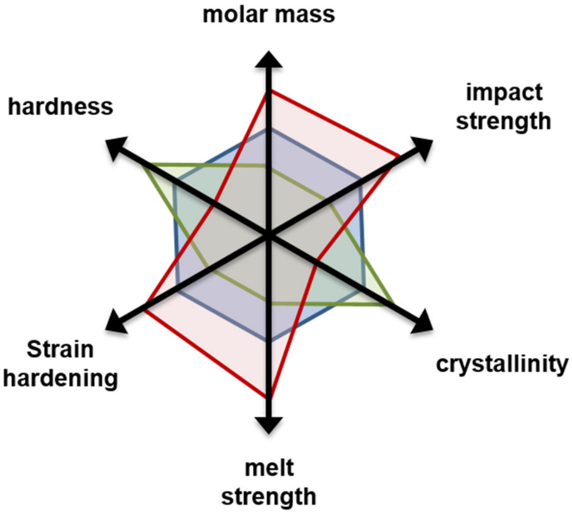

Fig. 2. Proposed improvements of PP properties (blue) by LCB (red) compared to mechanical Recycling (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Materials and methods

2.1. Materials

PP was collected from household post-consumer waste containing yoghurt, vegetable and beverage cups (thermoformed PP), boxes for rigid packaging (injection-moulded PP), bottle caps (injection-moulded PE-HD), and chewing gum containers and milk bottles (extrusion blow-moulded PE-HD). The material feedstock contained of 30% thermoformed PP, 60% injection moulded PP and 5% injection moulded PE-HD and 5% extrusion blow moulded PE-HD (rBlend). Furthermore, a single polymer waste fraction was sorted manually from thermoformed cups (rPP-cups). Complex viscosity and dynamic moduli of the raw materials are given in Fig. 3. As can be seen, the rheology data are in accordance with

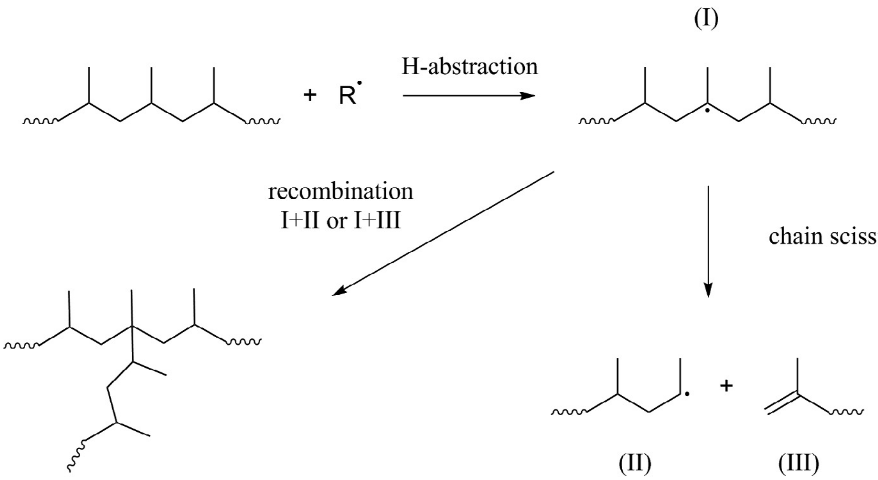

Fig. 1. General reaction scheme of the LCB formation.

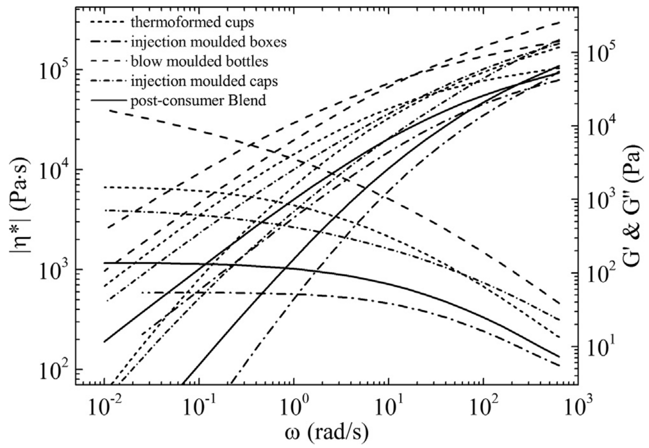

Fig. 3. Viscosity curves of the raw materials at 180 °C from post-consumer waste for this study.

the different fields of application, however, the recycled blow moulded PE-HD shows the highest complex viscosity (e.g. the viscosity ratio of the blow moulded PE-HD and injection moulded PP > 80:1), which has to be considered for mechanical testing.

Antioxidants for the stabilisation of commodity plastics can influence radical mediated melt functionalisation (Drooghaag et al., 2010). As a consequence, the isothermal oxidation induction time (OIT) was determined according to DIN ISO 11357-6 to compare the stabiliser effectiveness of the materials (DIN, 2013). The samples were heated up in open pans to 200 °C (10 K/min) under nitrogen atmosphere. Then the purging gas was changed to air and the temperature was kept at 200 °C for 90 min. Both recycled samples had OIT below 10 min, thus, as expected, a very low level of stabilisation can be concluded (Marshall et al., 1973) and side effect from antioxidants have not been considered for the discussion.

Styrene ($\geq$ 99%, Aldrich) was used without further purification. The peroxide Peroxan HX (2,5-Dimethyl-2,5-di-(tert.-butylperoxy)-hexane; 10 h half life time at 115 °C) and the PODIC Peroxan C126 (Di-tetradecylperoxydicarbonate; 10 h half life time at 48 °C) were supplied by Pergan. Irganox 1010 (Pentaerythritol tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)) was supplied by BASF and was used for heat stabilisation.

2.2. Sample preparation

A Fritsch granulator "Pulverisette 16" was used to produce flakes with a mean diameter of 3 mm. PP and PE-HD post-consumer waste were shredded separately. The chemicals (peroxide and monomer, or PODIC dissolved in n-hexane) were premixed and dropped on the polymer flakes, and stored overnight. Reactive extrusion was carried out in a Haake Mini Lab twin-screw extruder at 180 °C. Sample names and abbreviations are given in Table 1. For the tensile tests (ISO 527-2 type 5A) and the impact tensile tests (60 mm × 10 mm × 1 mm), specimens were injection moulded with a Haake Mini Jet at 230 °C melt- and 80 °C mould temperature. For the rheology measurements discs (25 mm diameter and 1.2 mm thick) and sheets (100 mm × 100 mm × 0.5 mm) were compression moulded at 180 °C and 25 bar.

Table 1
Sample specifications.

Sample	Sample specification
rPP-cups	PP from cups, extruded and stabilized
rPP-cups A1	20 mmol/kg peroxide, 480 mmol/kg styrene (5%)
rPP-cups A2	35 mmol/kg peroxide, 840 mmol/kg styrene (9%)
rPP-cups B	20 mmol/kg PODIC (1%)
rBlend	Post-consumer waste blend, extruded and stabilized
rBlend A1	20 mmol/kg peroxide, 480 mmol/kg styrene (5%)
rBlend A2	35 mmol/kg peroxide, 840 mmol/kg styrene (9%)
rBlend B	20 mmol/kg PODIC (1%)

2.3. Dynamic rheology

Dynamic rheology measurements were carried out on a plate-plate Anton Paar MCR 301 rheometer equipped with a CTD 450 heating chamber under nitrogen at 180 °C with 1 mm gap size. Frequency was chosen between 628 and 0.01 rad/s, deformation was raised from 1 to 2% logarithmically during the measurement. Deformation was in the linear viscoelastic range and thermal stability was proven at 180 °C for 2 h at constant conditions.

2.4. Extensional rheology

Stripes with 8 mm width for extensional rheology were cut from sheets after compression moulding. Extensional rheology was measured, using a Sentmanat Extensional Rheometer (SER-HPV 1) for Anton Paar rheometers, at 180 °C and five different strain rates ($\dot{\varepsilon}$ = 10 s^{-1}; 3 s^{-1}; 1 s^{-1}; 0.3 s^{-1}). The start-up curve was measured with a steady shear experiment at a plate-plate system and two different shear rates (0.001 s^{-1} and 0.1 s^{-1}).

2.5. Gel content

According to ASTM D 2765, 300 mg of the polymer were weighed into paper filters and refluxed in 100 ml xylene overnight to determine the insoluble gel content.

2.6. Tensile tests and tensile impact strength

The test machine (Zwick 050) was equipped with a 1 kN load cell and an extensometer, the test speed was 10 mm/min. Impact tensile test specimens were notched on both sides and tested according to ISO 8256 method A (2 J hammer; cross head mass = 15 g) on a Instron Ceast 9050.

3. Results and discussion

3.1. Rheology

Dynamic rheology makes a valuable contribution to the characterisation of polymer melts due to its high sensitivity with respect to long-chain branches (Stadler et al., 2006). In comparison to other analytical methods, it is the best common method to discuss molecular parameters (molar mass and molar mass distribution), the polymer architecture and relevant parameters for manufacturing (Mezger, 2016). The complex viscosity $|\eta*|$ of the modified and the unmodified single polymer waste are given in Fig. 4a and for the post-consumer blend in Fig. 4b. The $|\eta*|$ of rPP-cups and rBlend reach the zero shear viscosity η_0 under the given conditions. As expected, η_0 of rPP-cups is significantly higher than η_0 of rBlend. Thermoforming requires a higher melt strength to prevent sagging. To increase melt strength of linear PP the molar mass – and therefore η^0 – needs to be increased (Lau et al., 1998). The LCB modification reduces $|\eta*|$ at higher ω (shear thinning behaviour) and the transition from power law to zero shear viscosity regime becomes broader (increasing zero-shear viscosity). Both objections are characteristic for a change in molecular structure of the polymer, especially for branching (Gahleitner, 2001). According to (Zeichner and Patel, 1982) molecular changes of PP

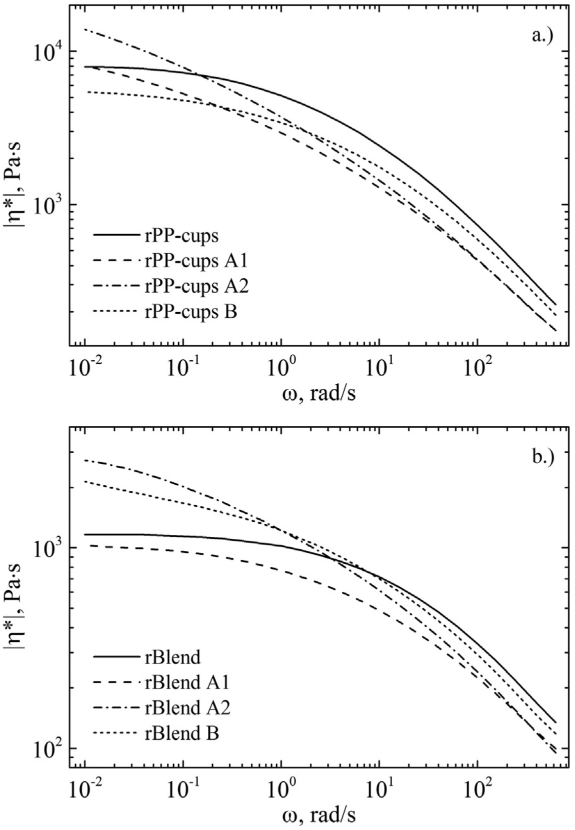

Fig. 4. $|\eta^*|$ of the modified and unmodified post-consumer waste blends (a) and the recycled cups (b).

can be discussed by the comparison of the crossover frequency ω_C and the crossover modulus G_C ($G' = G''$). A shift of ω_C to lower values indicates a growth, to higher values a decrease of molar mass. A higher G_C implies a narrowing of the molar mass distribution, a smaller G_C a broadening respectively (Fleissner, 1992). The values are given in Table 2.

According to the given results, the modification A1 reduces M_W and broadens MMD. A higher concentration of styrene and Peroxan HX (A2) results in a higher degree of grafting, which enhances the recombination reaction of the polymer chain (Wong and Baker, 1997). This leads to pronounced broadening of MMD and increased M_W compared to A1 modified samples. rBlend B shows a significant deviation in the low frequency regime and higher $|\eta*|$ at $\omega = 0.01$ than the rBlend.

According to (Braun et al., 1998; Chikhalikar et al., 2015), PE in a PP/PE-blend or in a PP/PE-copolymer can form highly branched networks during peroxide assisted chemical modification, which are insoluble in boiling xylene. Such networks can cause a second elastic plateau, which can be highlighted as second crossover point of the moduli or as a local maximum of tan(δ) (Fig. 5a and b). rBlend A1 and rBlend B show such a local maximum of tan(δ) caused by crosslinks of PE-HD.

Table 2
Summary of the rheological data from the frequency sweep.

Sample	ω_C [rad/s]	G_C [kPa]	Comment
rPP-cups	26	28.7	
rPP-cups A1	48	21.4	M_W ↓, MMD ↑
rPP-cups A2	22	15.3	M_W ↑, MMD ↑
rPP-cups B	47	29.2	M_W ↓, MMD ↓
rBlend	224	35.0	
rBlend A1	344	31.4	M_W ↓, MMD ↑
rBlend A2	194	23.9	M_W ↑, MMD ↑
rBlend B	332	21.5	M_W ↓, MMD ↑

For the proof of strain hardening, extensional rheology measurements with the SER extension tool were performed. The extensional viscosity (η^+_E) of rPP-cups (Fig. 6a) showed no strain hardening behaviour neither did η^+_E of the rBlend. However, it is noted that the rBlend showed significant sagging of the polymer stripe because its low melt strength (Fig. 6b), therefore it was not possible to determine η^+_E at low strain rates. The styrene modified samples (rPP-cups A1 and A2 and rBlend A1 and A2) show strain hardening which depends on the strain rate. Strain hardening is more pronounced at high than at low elongation rates. The PODIC modified sample rPP-cups B and rBlend B show strain hardening but no strain rate dependency. These results are in accordance to our previous work with virgin material.

3.2. Gel content

No gel was obtained for rPP-cups from single PP waste (Fig. 7). The result of rPP-cups A2 is lower as the detection limit of the standard. In case of the rBlend melt blending formed 3% of crosslinked gel, after modification B this value increased up to 12%. The gel content grows up to nearly 15% in rBlend A1 and decreases with increasing styrene and peroxide content in rBlend A2. Formation of gel in PODIC modified rBlend B is within the expected range.

3.3. Tensile and impact tensile tests

The tensile tests in Fig. 8 show a good improvement of the elongation at break with the PODIC modified single PP waste (rPP-cups

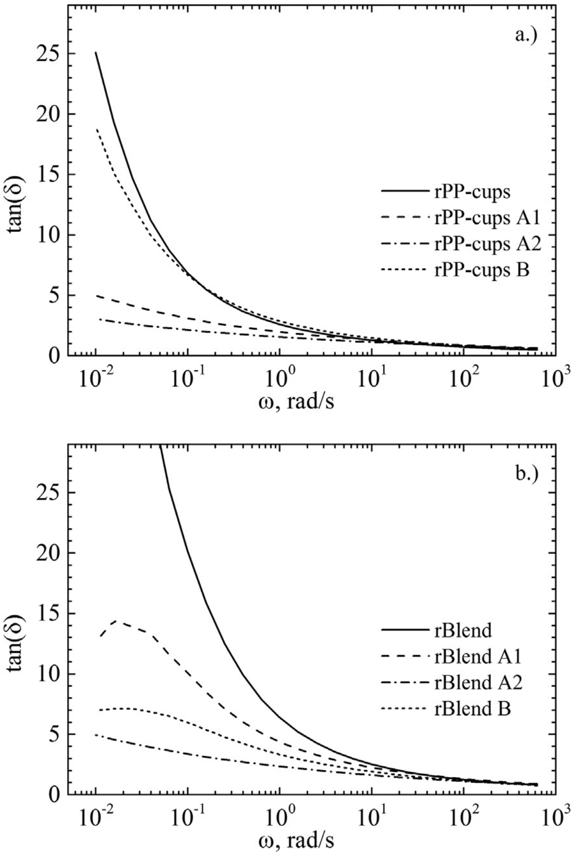

Fig. 5. tan(δ) of the modified and unmodified the recycled cups (a) and post-consumer waste blends (b).

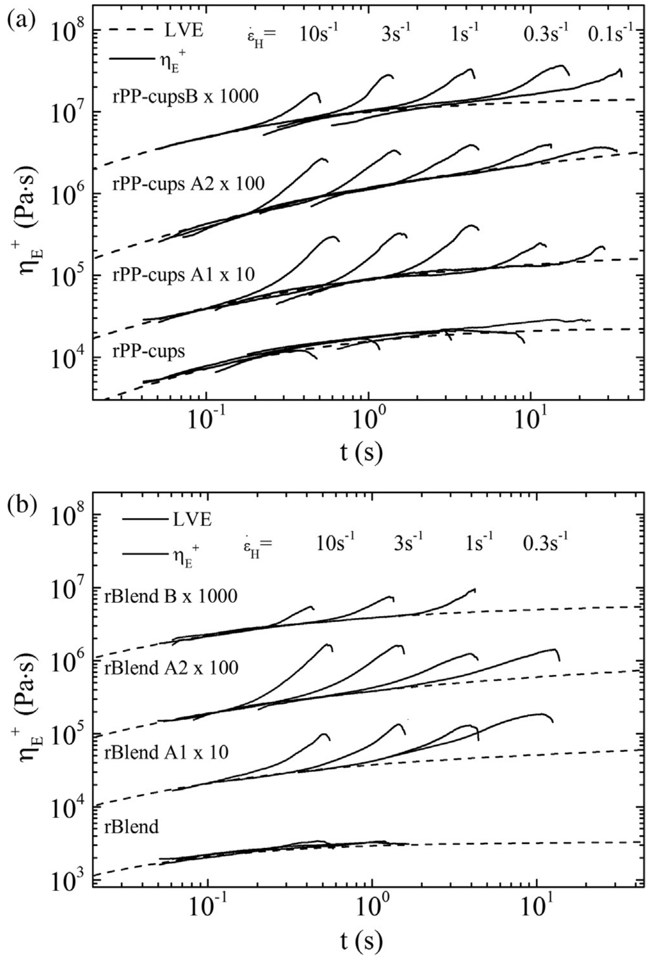

Fig. 6. Extensional viscosity curves for rPP-cups and of the post-consumer blend.

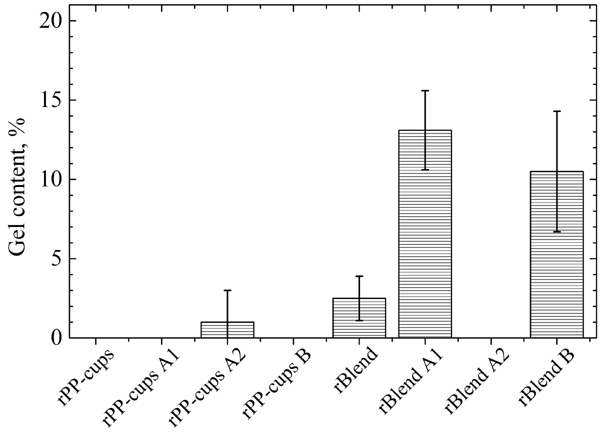

Fig. 7. Gel content of modified and unmodified rPP-cups and of the post-consumer waste blends.

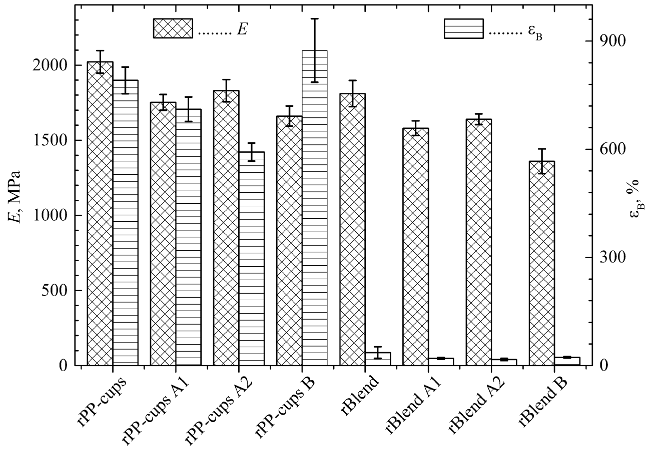

Fig. 8. Tensile tests of modified and unmodified single polymer waste PP and of the post-consumer waste blends.

B). Modification with styrene reduces the elongation at break (rPP-Cups A1). This effect intensifies with a higher styrene content (rPP-Cups A2). rBlend, however, had a weak performance for modified and unmodified samples. It is obvious that LCB was not able to compensate the crosslinking side reaction, so elongation at break was not improved. The trend of the modulus curves is similar for both feedstock materials and the smallest values for the tensile modulus were obtained with PODIC for LCB. Additionally, the dispersed PE-HD influences the morphology and the mechanical properties negatively, due to the unfavourable ratio of matrix and dispersed phase viscosity. According to (Wu, 1987) the size of the drops of the dispersed phase is directly proportional to the ±0.84 power of the viscosity ratio. The drops are smaller when the ratio is closer to unity. This limitation could not be reached with the composition of rBlend (already the viscosity ratio of blow moulded PE-HD and injection moulded PP > 80:1).

In our previous work, an increase of impact tensile strength of a PODIC modified PP/PE-blend was shown. We suggested that PODIC delays PE-HD crosslinking in a similar way a Quinone does, which resulted in an increased impact strength (Chodak, 2004). However, these observations were not found for rBlend B. rBlend, rBlend A1 and rBlend A2 have a low impact resistance (Fig. 9). The impact tensile strength is influenced by the monomer (styrene reduces toughness) and by the LCB. As the impact tensile strength of the unmodified material rPP-cups was already quite high, modification with PODIC brought no further improvement.

4. Conclusion

Two selected fractions from plastic household post-consumer waste were "up-cycled" by chemical modification using styrene and peroxide and a peroxydicarbonate (PODIC), which results in a long chain branched (LCB) structure. The formation of LCB was detected by dynamic and elongational viscosity measurements.

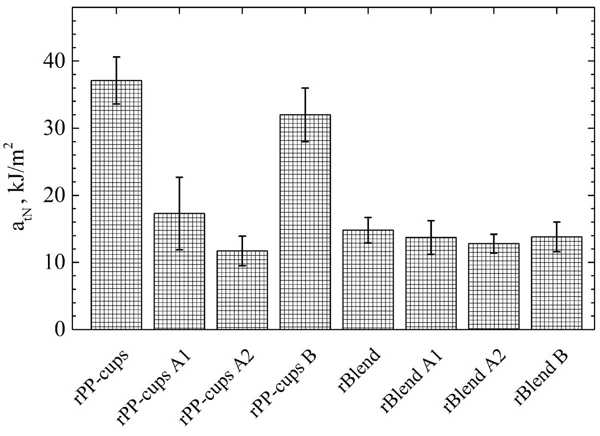

Fig. 9. Impact tensile tests of the single polymer waste PP and of the post-consumer waste blends.

Apparently, a mixed polyolefin waste system has two crucial limitations. First, cross-linking reactions of the PE-HD occur during a peroxide-induced chemical modification like LCB. The gel formation in the blend containing 10% PE-HD as impurity can be implied from changes in dynamic moduli and the complex viscosity after modification and was proven by a gel content determination according to ASTM standard too. Second, the viscosity profile of commingled polyolefin waste (even with only 10% PE impurity) with no continuous composition has to be considered. The dispersed PE-HD is expected to influence the morphology and the mechanical properties negatively, due to the unfavourable viscosity ratio of matrix and dispersed phase viscosity. These unfavourable certainties explain the significant deterioration of the elongation at break (material failure below 100% elongation) and the impact tensile strength. Consequently, the necessity of a single polymer fraction for recycling remains as criteria for a high quality product.

The single polymer waste fraction (rPP-cups), which was collected from thermoformed cups, showed results within the expected range comparable to virgin material (strain hardening and improved elongation at break) and therefore no limitations for a possible "up-cycling"-process. Furthermore, the introduction of strain hardening behaviour and the increase of the melt strength were not influenced by the aforementioned side effects in the blend containing 10% PE-HD and are in accordance to former results with model mixtures.

Compared to common mechanical recycling, the "up-cycling"-process presented involves only one additional manufacturing step namely the addition of the chemicals before the re-extrusion. From the current status of knowledge the chemicals for the "up-cycling" step would increase the manufacturing costs by 30–50% (0.30 €/kg estimated costs for processing of sorted flakes and for the chemicals 0.1 €/kg (A1), 0.15 €/kg (A2) and 0.14 €/kg (B) respectively). A more accurate estimation of the costs is not possible now. But the up-cycled PP will not have to compete with the product costs of virgin PP, but with a price 60% higher for HMS-PP.

Nonetheless, the environmental impact of the used chemicals has to be considered. The styrene and the peroxide will affect the production costs (removing of volatiles), but such a procedure is common for some HMS-PPs (e.g. Daploy™). Apart from a cooled storage, the PODIC is harmless and a post-manufacturing treatment is not necessary. The resulting up-cyclate is expected to have at least the same ecological impact like a comparable commercial HMS-PP. However, a complete life cycle analysis is necessary and will be the part of future work.

The improved material properties from the introduction of strain hardening behaviour and increasing melt strength offer the possibility to produce blown films and PP foams. Thereby the application profile of the PP post-consumer waste is expanded. As a result, LCB of a single polymer waste fraction – even after more cost intensive sorting – is promising to have a recycling net benefit instead of net costs and will help to implement an innovative up-cycling process for PP.

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Article

Influence of the Molar Mass on Long-Chain Branching of Polypropylene

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Abstract: Long-chain branching (LCB) with peroxydicarbonates (PODIC) is known as a suitable post-reactor process to introduce strain-hardening behaviour and an increase of melt strength to a linear polypropylene (PP). This opens up new possibilities for processing and therefore application. Especially in the case of adding value to PP post-consumer waste, LCB is a promising approach. LCB takes place by a combination of chain scission and recombination after radical activation of the PP macromolecule. However, chemical modification of post-consumer waste is challenging because of the inhomogeneous composition and the manifold number of PP grades. The influence of the molar mass of the linear PP precursor on this reaction was studied with different PP grades ranging from extrusion grade to injection moulding grade. To exclude side effects, all PP grades had similar polydispersity indices. A PP with higher molar mass undergoes significant chain scission during the LCB process compared to a PP with low molar mass for injection moulding. Therefore, the two grades differ significantly in their branching number, which influences their behaviour in elongational flow.

Keywords: long-chain branching; polypropylene; recycling

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1. Introduction

Isotactic polypropylene (PP) is one of the most popular consumer plastics in the global polymer market. Its applications include plastic pipes, injection-moulded building parts, chill-rolled and blow-moulded films, fibres, thermoforming, etc. Regarding other thermoplastics, PPs' desirable properties like low density, high melting temperature, moderate stiffness and low cost make it the plastic with the second largest share in global plastic production [1,2]. Conspicuously, most applications of PP are designated only for short-term single use. As a result, a big share of the produced PP ends up quickly in post-consumer plastic waste. Establishing viable recycling processes is still a challenge as most PP post-consumer waste is incinerated or goes to landfill [3].

Mechanical recycling requires reliable analytical methods for quality assessment but would be the method of choice for the reintroduction of post-consumer waste PP in the manufacturing process of new PP products [4]. For example, the recycling of lead and PP from car batteries is a successful concept [5]. However, these processes are limited as PP is prone to photo-oxidation and degradation processes during its lifetime and mainly during the re-processing procedure due to the presence of tertiary carbons [6–9]. PP post-consumer waste collected from municipal household waste is a commingled feedstock with irregular composition. The impurities in PP post-consumer waste can be categorised into four groups: high molecular impurities like other plastics; low molecular impurities like different stabilisers; homo molecular impurities like PPs with different molar masses, or *co*-polymers; and inorganic impurities like fillers or metals [10,11]. While plastics with significant higher densities like polyethylene terephthalate (PET) and polyvinylchloride (PVC) can be separated by flotation in water, the similar densities of polyethylene (PE) and PP impede a simple separation [12]. For the reuse of PP/PE-fractions, compatibilisers like ethylene-propylene-rubber (EPR) are added to reduce negative influences from the immiscibility of PE and PP [13,14]. In the literature, concepts like in situ compatibilisation of PP/PE blends are shown to be attractive and cheap alternatives. Reactive monomers and/or peroxides are used to generate interfacial crosslinks to improve the mechanical properties of the polyolefin blends [15–22]. The kinetics of such grafting reactions is of great interest and so they have been studied intensively. A novel kinetic Monte Carlo strategy was recently presented by Hernández-Ortiz et al. to model the event history of grafting reactions [23].

In order to introduce long-chain branches (LCB) in linear isotactic PP, similar combinations of monomers and peroxides are used. LCB is a well-studied topic in the literature and numerous possibilities have been offered to find an efficient process to compensate for the loss of mechanical properties during recycling [24–34]. LCB in general results in an increase in the molar mass, a broadening of the molar mass distribution, an acceleration of crystallisation and an increase of the melt strength as well as strain hardening [34–38]. In case of PP, the property profile is extended due to the increased melt strength and special product applications, such as foaming and film blowing [39]. A suitable method to get LCB-PP from a linear isotactic PP homopolymer was presented by Lagendijk et al. They used peroxydicarbonates (PODIC), a special class of peroxides, to generate PP with an LCB structure [40]. PODICs with long aliphatic side chains (e.g., di-myristyl-peroxydicarbonate) are well described in a later work to give a high branching efficiency [41]. The PODIC acts as both initiator and *co*-agent and mediates partial chain scission and radical stabilisation for a successful branching reaction. A general reaction scheme is given in Figure 1.

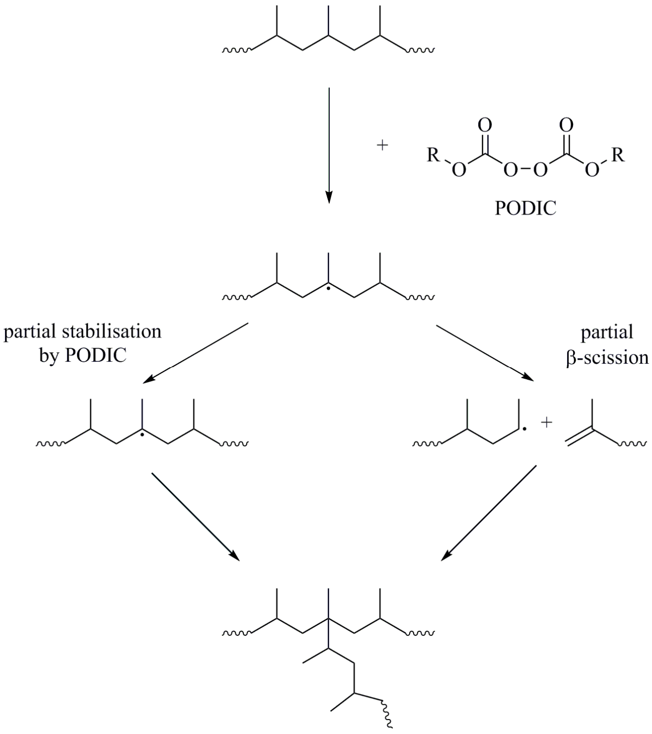

Figure 1. Reaction scheme of LCB process assisted by PODIC, according to Lagendijk et al.

A detailed study of the PODIC-mediated LCB reaction in melt has not been provided yet. In general, two alkoxy carbonyloxyl radicals are formed by a homolytic cleavage of the O–O bond

(II). In case of a sufficiently long time interval, (II) may decarboxylate by eliminating carbon dioxide, producing two alkoxy radicals (III) (Figure 2). In the case of di-myristyl-peroxydicarbonate, Buback et al. showed a high stability of species (II) [42]. Species (III) is expected to abstract hydrogen from the PP generating the PP macroradical. The improvement in melt strength is ascribed to the stabilisation of the PP macroradical due to the recombination with (II) and the formation of an alkylcarbonate-polymer adduct [43].

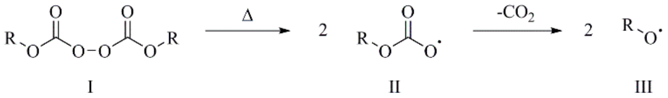

Figure 2. Decomposition of PODIC.

It could be shown that LCB is a suitable concept to improve the melt properties of PP from post-consumer waste with PE impurities, which is why one can speak of a real upcycling process [44]. The method of using PODIC and reactive extrusion is of special interest as it may be applied directly by the plastic manufacturer on recycled linear PP. However, LCB as an innovative recycling process is more promising when used for the modification of single polymer waste, because impurities like PEHD in PP post-consumer waste limit the number of possible applications of the upcycled product [45]. Nevertheless, even recycled single-polymer waste is a commingled resource of inhomogeneous composition. On the one hand, thermally and mechanically degraded PP resulting from reprocessing procedures has a high MFI, which influences the mechanical and flow properties [46,47]. On the other hand, single PP post-consumer waste contains different PP grades from different applications and therefore PPs with different molar masses. The molar mass is an important factor for the physical and mechanical properties of a polymer. For semi-crystalline thermoplastics, a higher molar mass induces an increasing number of inter- or intramolecular entanglements, a higher number of secondary bonds per volume, and changes of near- and long-range order. This directly influences the ability to crystallise, the elastic modulus and stiffness above glass transition temperature, as well as the flow properties in melt [48]. Therefore, the influence of PP grades of different molar mass on the LCB reaction and the number of LCB according to Lagendijk et al. in relation to the molar mass will be the topic of this study. In order to exclude any confounding effect of polydispersity, samples with similar M_w/M_n ratios were used.

2. Experimental Section

2.1. Materials

Four different isotactic PP homopolymers supplied by Borealis (Vienna, Austria) were used for the study. PP 1 (HA 104E, Borealis, Vienna, Austria) is a high molar mass extrusion grades for pipe systems, PP2 (HC 600TF) is intended for thermoforming applications, PP3 (HD 601CF, Borealis, Vienna, Austria) is a film resin for chill roll processes, and PP4 (HF 700SA, Borealis, Vienna, Austria) is a PP grade for injection moulding. The different PPs differ only in their molar mass (M_w and M_n), but have similar dispersities (M_w/M_n). Their rheological and molecular data are summarised in Table 1.

Table 1. Rheological and molecular data of the PPs used as raw materials for the study.

Sample	MFI [a] [g/10 min]	η_0 [Pa·s]	M_w [kg mol^{-1}]	M_n [kg mol^{-1}]	M_w/M_n
PP1	0.75	56 600	559	321	1.74
PP2	2.8	17 700	394	198	1.99
PP3	8	5 900	300	151	1.99
PP4	21	2 140	227	99	2.29

[a] provided in the product data sheet.

PODIC (a white powder) Peroxan C126 (Pergan, Schlavenhorst, Germany) (Di-tetradecylperoxydicarbonate; 10 h half-life at 48 °C) was supplied by Pergan (Schlavenhorst, Germany).

2.2. Thermal Analysis

A standard procedure with TA Instruments (TA) standard aluminium pans (5 mg sample mass) on a TA Q2000 DSC (TA instruments, Newcastle, DE, USA) was used for thermal analysis. Samples were heated to 200°C (10 $°\mathrm{C}\cdot\mathrm{min}^{-1}$), cooled down to room temperature and heated up again to 200 °C at the same rate. TA Universal analysis software (TA instruments, Newcastle, DE, USA) was used to determine melting (T_m) and crystallisation temperature (T_c), as well as the melting enthalpy (ΔH_m).

Oxidation induction time (OIT) was determined according to DIN ISO 11357-6 [49]. The samples were heated up in open pans to 200 °C (10 $°\mathrm{C}\cdot\mathrm{min}^{-1}$) under a nitrogen atmosphere. Then the purging gas was changed to air and the temperature was kept at 200 °C for 90 min.

2.3. Molar Mass Determination

The determination of the molar mass distribution (MMD) was carried out on a Viscotek High Temperature size exclusion chromatography (HT-SEC) system (Malvern instruments, Herrenberg, Germany) at 140 °C with 1,2,4-Trichlorobenzene as eluent and standard triple detection (refractive index, low angle light scattering and capillary viscometer).

2.4. Rheology

Discs with 25 mm diameter and 1.2 mm thickness for dynamic rheology were compression moulded at 20 bar and 180 °C. Dynamic rheology measurements were carried out on a plate-plate Anton Paar MCR 301 rheometer (Anton Paar, Graz, Austria) equipped with a CTD 450 heating chamber (Anton Paar, Graz, Austria) under nitrogen at 180 °C with 1 mm gap size. The frequency range was set from 628 to 0.01 $\mathrm{rad}\cdot\mathrm{s}^{-1}$ and deformation was raised logarithmically from 1% to 2% during the measurement. All measurements were performed within the linear viscoelastic region and thermal stability was checked by time sweep experiments at 180 °C for 2 h. The zero-shear viscosity η_0 of the samples was determined by measuring the creep compliance at 180 °C at a constant stress τ of 5 and 30 Pa. For small stresses, there is a linear range, whereby the creep compliance $J(t,\tau)$ reaches a stationary state and the zero-shear viscosity can be determined from the plateau of t/J when it is plotted against t.

$$\eta_0 = \lim_{t\to\infty}\left(\frac{t}{J(t,\tau)}\right) \tag{1}$$

This is shown in Figure 3 for PP1 and PP1-LCB.

2.5. Extensional Rheology

Stripes with 8 mm width for extensional rheology were cut from 100 mm × 100 mm × 0.5 mm sheets after compression moulding at 180 °C. Extensional rheology was measured using a Sentmanat Extensional Rheometer (SER-HPV 1, Xpansion instruments, Tallmadge, OH, USA) for Anton Paar rheometers, at 180 °C and five different strain rates ($\dot{\varepsilon}$ = 10; 3; 1; 0.3; 0.1 s^{-1}). The strain hardening ratio SHR was calculated using the maximum value of the elongational viscosity η^{+}_{Emax} for every strain rate and the corresponding value at time t from the threefold of the linear viscoelastic start up curve.

$$SHR = \frac{\eta^{+}_{\mathrm{Emax}}(t,\dot{\varepsilon})}{3\eta^{+}(t)} \tag{2}$$

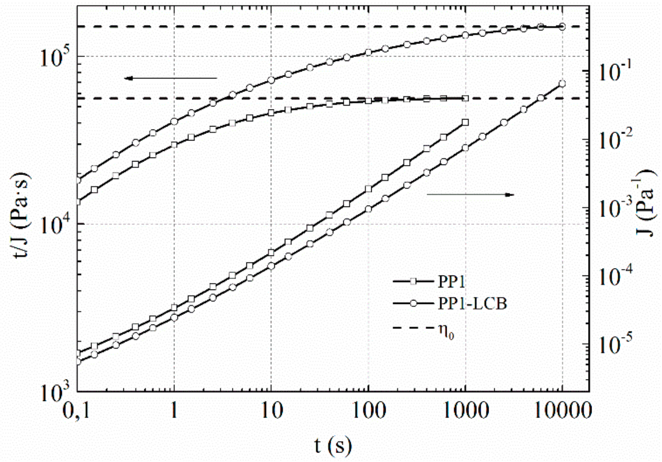

Figure 3. Creep experiments and determination of η_0.

2.6. Sample Preparation

Particles with a mean diameter of 1 mm were formed by shredding virgin PP granules with a Fritsch granulator "Pulverisette 16, Fritsch, Idar-Oberstein, Germany". From the literature it is known that stabiliser systems (especially hindered amine light stabilisers and sulphur-containing additives) can influence the melt modification of PP [28,50]. Therefore, the oxidation induction time (OIT) of the polypropylene grades was determined to compare the oxidative behaviour of the materials. PP1 for pipes and PP4 for injection moulding had an OIT longer than 90 min (Figure 4). To minimise possible side effects, the stabilisers were washed out of the grinded polymers PP1, PP2 and PP3 by Soxhlet extraction overnight with acetone. In the case of PP4, it was necessary to repeat the procedure with dichloromethane. The OIT of the industrial grade and after Soxhlet extraction are summarised in Table 2.

A solution of the PODIC in 50 ml *n*-hexane was purified on the destabilised grinded polymer, mixed and then stored at room temperature until the solvent evaporated. Reactive extrusion was carried out in a Haake Mini Lab II conically shaped twin-screw extruder at 180 °C and with 100 rpm screw speed for 5 min. After 4 min, when the PODIC should be completely decomposed (estimated from the half-life), 1 mg (about 0.02%) Irganox 1010 (BASF, Ludwigshafen, Germany) was added in order to prevent further degradation.

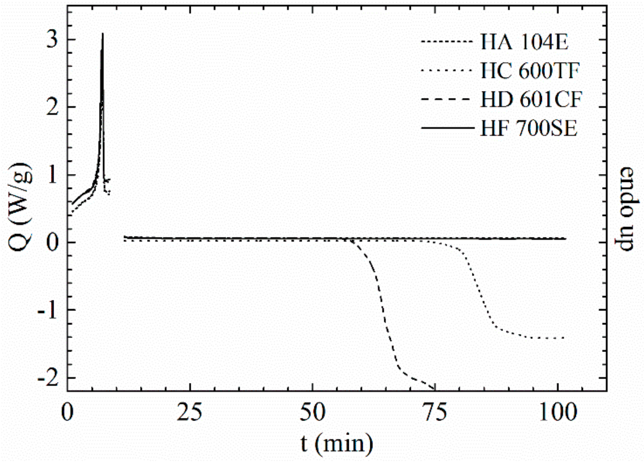

Figure 4. Comparison of the OIT of the shredded PP granules.

Table 2. OIT before and after Soxhlet extraction of the PPs.

Sample	OIT Industrial Grade [min]	OIT after Soxhlet [min]
PP1	>90	17
PP2	67	9
PP3	48	10
PP4	>90	11

3. Results and Discussion

3.1. Thermal Analysis

The degree of crystallinity of semi-crystalline polymers depends—besides the processing conditions—on the molar mass and the structural regularity of a given polymer. It can be reflected by the enthalpy of fusion ΔH_m, and the melting temperature T_m and is reduced by the introduction of non-crystallising structural units such as branches and grafts [48]. During the radical induced melt modification of PP, degradation and recombination take place simultaneously, which results in a higher M_w, a broadening of MMD and more chain irregularity. Therewith the crystallisation behaviour of the LCB-PP is affected. Wang et al. described the crystallisation behaviour of LCB-PP prepared by grafting of pentaerythritol triacrylate (PETA). They suggested that the small number of branching points in LCB-PP increases the nucleation density, which results in higher T_c [51]. Compared to its linear precursor, Tian et al. calculated smaller Avrami exponents for LCB-PP, which was also prepared by grafting with PETA. They concluded that LCB acts as a heterogeneous nucleating agent and influences the mechanism and the growth of PP crystals [52]. Also, Nam et al. suggested irregularities induced by long-chain branching to broaden the melting peak of the LCB-PP [39]. Tabatabei et al. studied blends of linear and LCB-PP, and postulated that even a small amount of LCB increases the number of nuclei sites, resulting in an increase of crystallinity. However, an increased number of branches prevents chain mobility, leading to a decrease in crystallinity (20% of LCB-PP in the blend) [53]. Nevertheless, ΔH_m, T_m and T_c increased for all samples (shown in Figure 5).

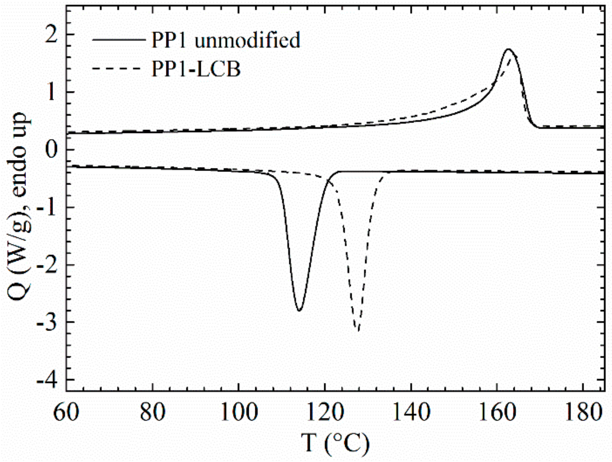

Figure 5. Changes in thermal properties for linear and LCB-PP1.

The extent of the increase of ΔH_m, decreases from PP1-LCB over PP2-LCB and PP3-LCB to PP4-LCB and therefore so does the effect of PODIC modification on the crystallisation behaviour.

As can be seen in Table 3, the extent of the increase of ΔH_m decreases from PP1-LCB over PP2-LCB and PP3-LCB to PP4-LCB. Therefore, the effect of PODIC modification on the crystallisation behaviour is more pronounced in a high molar mass grade PP compared to the injection-moulding grade, with an innately high ability to crystallise.

Table 3. Thermal properties of the studied polymer samples.

Sample	T_m [°C]	T_c [°C]	ΔH_m [J·g^{-1}]
PP 1	163	114	90
PP 1-LCB	164	128	98
PP 2	161	113	92
PP 2-LCB	163	128	98
PP 3	162	115	93
PP 3-LCB	163	128	99
PP 4	162	114	98
PP 4-LCB	163	127	101

Further conclusions relating changes of the polymer structure (e.g., an average number of branches per molecule) cannot be drawn from the DSC data, but it is a fast and reliable method and gives a hint of the success of the LCB reaction.

3.2. MMD and LCB of the PP Samples

The weight average molar mass, the number average molar mass, and the polydispersity indices and the number of branches per molecule are summarised in Table 4. The MMD of all polymer samples is shown in Figure 6. The LCB samples (dashed lines) show a distinctive shoulder in the high molar mass region. This shoulder looks more pronounced when the linear PP has a higher molar mass. M_w and M_w/M_n thus increased for all samples. Additionally, the peak maximum of the MMD of PP1-LCB was distinctively reduced and the peak also broadens in the region of smaller molar masses.

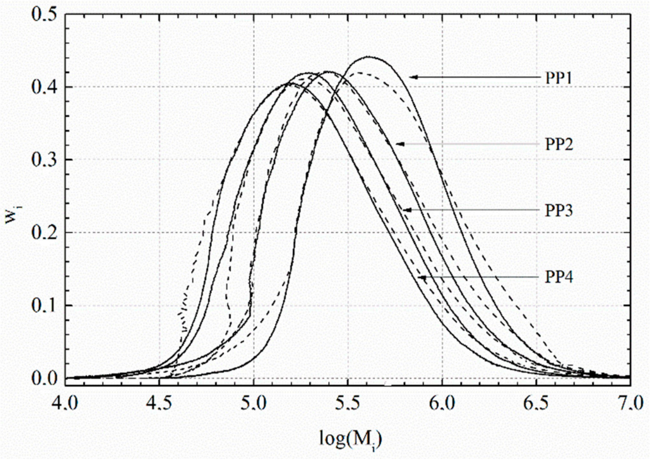

Figure 6. MMD of the linear PP samples (compact lines) and the LCB samples (dashed lines).

The branched structure of the LCB-samples can be detected from the Mark–Houwink plot in Figure 7, by comparing the solution of the LCB-sample with its linear precursor under the condition of a similar molar mass. Comparison with a linear equivalent should also enable the quantification as well as the detection of branching. In Table 4, the average number of branches per molecule B_n was calculated according to the model of Zimm and Stockmeyer [54,55], using the method of Lecacheux et al. [56]. This method has a number of limitations, but allows for an accurate quantification of branching, e.g., for PE [57,58], and is therefore also commonly used for PP.

$$g = \left(\frac{[\eta]_b}{[\eta]_l} \right)^{\frac{1}{\epsilon}} \tag{3}$$

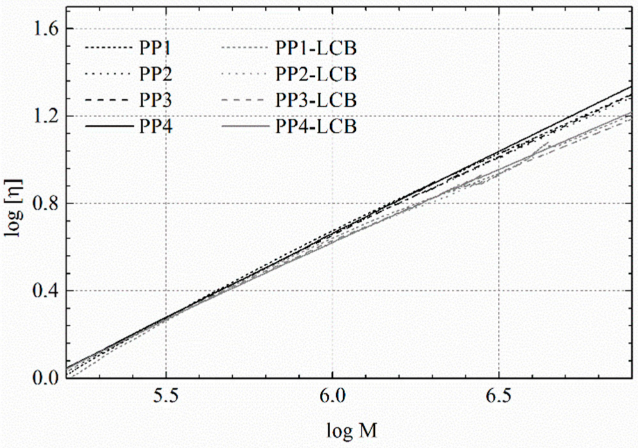

Figure 7. Intrinsic viscosity as a function of the molar mass of the linear PPs (black lines) and the LCB PPs (grey).

The ratio of the mean square radii of gyration g was calculated from the intrinsic viscosity of the branched $[\eta]_b$ and the linear $[\eta]_l$ polymer. The parameter ϵ depends on the type of branched structure and the solvent–polymer interaction. In the literature, ϵ has a value of 0.5 for star polymers, 1.5 for combs with large backbones and short branches, and 0.7 for multi-arm stars [59–61]. For LCB-PP a value of ϵ = 0.75 is often used in the literature [40,62,63]. B_n was calculated by solving the following equation and the results are summarised in Table 4:

$$g = \left[\left(1 + \frac{B_n}{7} \right)^{\frac{1}{2}} + \frac{4B_n}{9\pi} \right]^{-\frac{1}{2}}. \tag{4}$$

Table 4. Molar masses, polydispersity and branching number of the LCB-PPs.

Sample	M_w [kg mol^{-1}]	M_n [kg mol^{-1}]	M_w/M_n	B_n
PP1-LCB	611	317	1.92	0.08
PP2-LCB	436	196	2.22	0.13
PP3-LCB	333	151	2.20	0.25
PP4-LCB	264	106	2.49	0.27

The results in Table 4 show that B_n increases, with a decrease of the molar mass of the linear PP. According to the reaction scheme in Figure 1, PP1 (with high molar mass) forms larger chain fragments with reduced ability for recombination during LCB due to lower chain mobility, which is in accordance with [64]. This results in a decreasing branching number B_n and longer side arms with a higher molar mass. The prevalence of LCB (and increasing B_n) seems enhanced, with a lower molar mass of the linear unmodified PP.

3.3. Dynamic Rheology

The linear viscoelastic behaviour of a polymer melt is sensitive to structural changes of macromolecules, especially to LCB. Therefore, the comparison of dynamic moduli is a well-established technique to show the structural changes of a polymer. LCB primarily influences the elastic behaviour and therefore the storage modulus of the polymer samples in the low-frequency regime. The storage moduli of linear precursors and the LCB-PPs are presented in Figure 8. According to the predictions of Fleissner et al., changes in M_w and MMD (e.g., induced by the LCB) influence the position of the modulus crossover point [65]. The crossover modulus of all samples decreases with LCB (broadening of MMD) and the crossover frequency shifts towards smaller values (higher M_w). Except for PP1, its crossover frequency shifts towards a slightly higher value (smaller M_w), which is in accordance with the data from SEC.

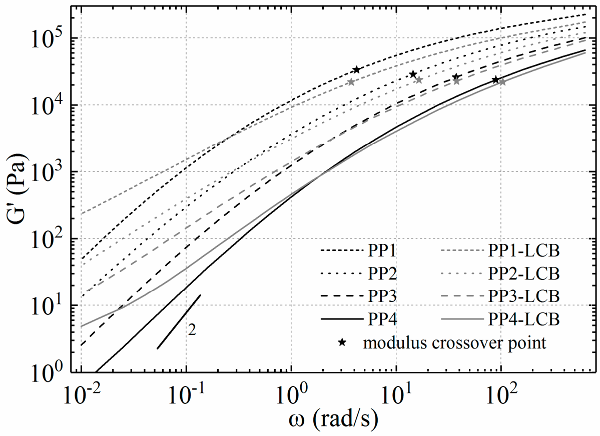

Figure 8. Storage moduli as a function of angular frequency at 180 °C.

Additionally, the storage modulus of PP4-LCB shows a clear and PP3-LCB a slight deviation from the slope of 2 in the low frequency range, which may include a second elastic plateau. According to Wood-Adams [61], such a second plateau is a further hint of the branched structure of the measured polymer. A plot of the loss angle δ and the complex modulus $|G^*|$ (van Gurp Palmen plot) offers the possibility to classify and quantify the amount and type of LCB with a linear reference of similar MMD [66,67]. The deviation from the linear reference depends strongly on the degree of LCB (which is shown in Figure 9 for PP2 and PP2-LCB). In our case a lightly LCB structure can be concluded from the plot.

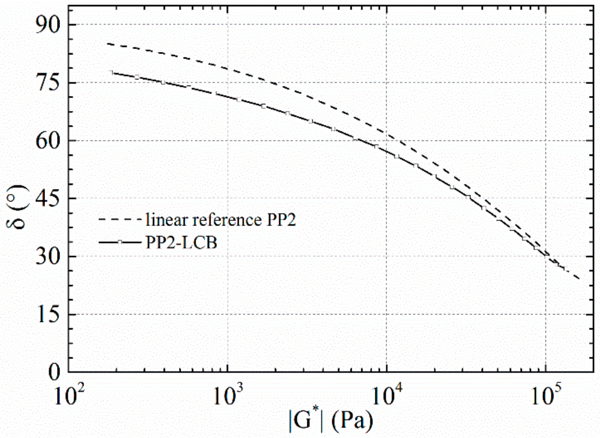

Figure 9. δ-$|G^*|$-plot of PP2 (linear reference) and PP2-LCB.

Further characteristic effects of a branched structure, when compared to a linear precursor, are a pronounced shear thinning at high shear and a higher viscosity at low shear. As can be seen in Figure 10, the linear PPs reach their zero-shear viscosity plateau between the frequency of 0.1 rad·s^{-1} and 1 rad·s^{-1}, while the transition zone from power law to the zero-shear regime shifts to smaller frequencies and becomes broader for the LCB-PPs. The effect of shear thinning is more pronounced with PP1-LCB and decreases with diminishing molar mass.

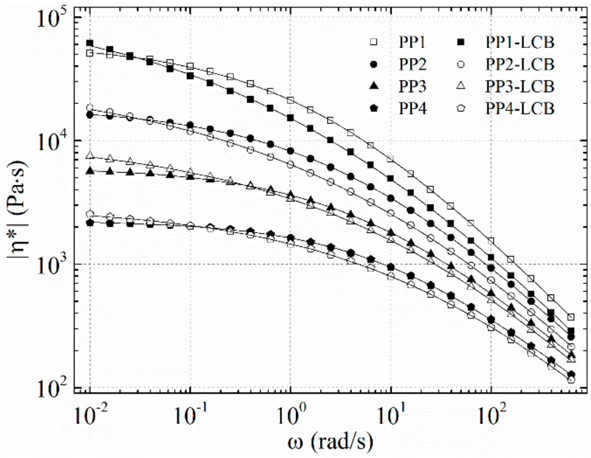

Figure 10. Dynamic viscosity as a function of angular frequency at 180 °C and the prediction of the Carreau–Yasuda model.

According to Tsenoglu et al., the branching number B_n can also be calculated from the measured zero-shear viscosity of the branched PP η_b and the linear PP η_l, especially for LCB-PP prepared from a linear PP with PODIC [68]. The theory assumes that for sparsely branched polymers the number of branch points per molecule is either zero or one, and the melt is approximated to a blend of mostly linear with three-arm star-shaped chains with arm length half of the average length of the linear precursor. Under these assumptions, the fraction of branched molecules equals B_n, which can be calculated with Equation (5):

$$B_n = \frac{\ln\left\{\frac{\eta_b}{\eta_l}\right\}}{\alpha\left[\frac{M_L}{M_C} - 1\right] - 3\ln\left\{\frac{M_L}{M_C}\right\}}. \tag{5}$$

In this equation M_L is the weight average molar mass of the linear PP, M_C the molecular weight at the onset of entanglements, which is equal twice of the molecular weight of two successive entanglements ($M_C \approx 2M_e$), and the numerical coefficient $\alpha = 0.42$. According to the tube model, $\alpha = 15/8$, but experiments indicated a lower value of $\alpha \approx 0.43$–0.60 for star-shaped polymers [68]. In a later work, Gotsis et al. used a modified $\alpha = 0.48$ for a LCB-PP with lower molar mass compared to their previous work and postulated that α is dependent on the molar mass and the molar mass distribution [35]. For PP1-LCB and PP2-LCB results of B_n were obtained with $\alpha = 0.42$ similar to B_n from HT-SEC. For PP3-LCB and PP4-LCB $\alpha = 0.42$ gave no satisfying results. Jørgensen et al., for example, needed to adapt $\alpha = 0.8$ to get the best fit for their LCB-metallocene HDPE [69]. We also used adapted α values to get the best fit for PP3-LCB and PP4-LCB (results are shown in Table 5). However, the values are within the experimental values of $\alpha \approx 0.43$–0.60, which are given in the literature.

Table 5. Branching number from rheological data.

Sample	η^0 [Pa·s]	B_n	α
PP1-LCB	150 200	0.08	0.45
PP2-LCB	37 100	0.13	0.46
PP3-LCB	11 500	0.25	0.49
PP4-LCB	2730	0.27	0.52

3.4. Extensional Rheology

Distinct differences in the elongational behaviour are related to changes in the molecular structure of the studied PP. LCB-PPs are able to build up a strong entangled network connected with strong nonlinear effects of the elongational viscosity called strain hardening. As can be seen in Figure 11, the linear PPs show no strain-hardening behaviour and no deviation from the linear viscoelastic start-up curve. Because of the low zero-shear viscosity of PP4 at the measuring temperature, it was not possible to measure the extensional viscosity at Hencky strain rates below 1 s^{-1}.

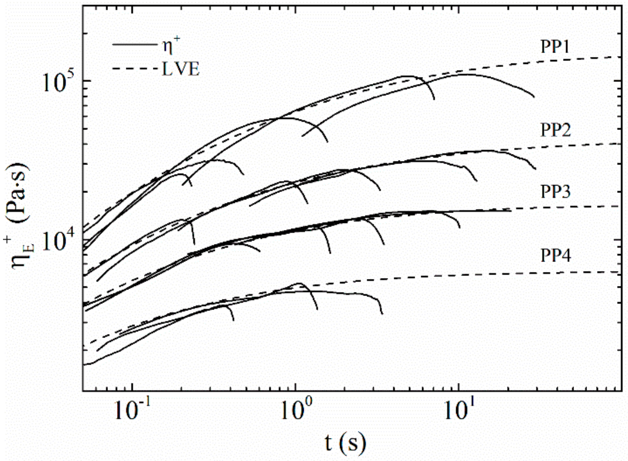

Figure 11. Extensional rheology of the linear PPs.

The modification with PODIC induced LCB to the linear polymer backbone and therefore strain-hardening behaviour was obtained for all LCB-PPs. (It has to be noted that PP3-LCB and PP4-LCB show slight sagging, which is, especially at lower strain rates, in competition with the strain hardening.) The SER curves are plotted in Figure 12 and the calculated corresponding strain-hardening ratios are given in Figure 13. The SHR increases with increasing B_n, which can be seen in Figure 13 when the SHR at ε = 1 s^{-1} of PP1-LCB, PP2-LCB and PP3-LCB are compared. This is in agreement with the results from HT-SEC and the calculated B_n. All samples show a dependency of the strain hardening on the strain rate. The SHR of PP1-LCB shows a slight decrease of SHR with increasing strain rate; this becomes clearer for PP3-LCB. The SHR of PP3-LCB and PP4-LCB first increase and reach their maximum at ε = 1 s^{-1} and then decrease again. According to Gabriel et al. [70], more pronounced strain hardening at the lower Hencky strain rate is a sign of fewer branches in the polymer, which is in agreement with the calculated B_n. However, PP3-LCB and PP4-LCB do not exactly follow the observations from Gabriel at al. but lie between the predictions. This seems obvious because the B_n for PP3-LCB and PP4-LCB are not enough so speak from highly branched.

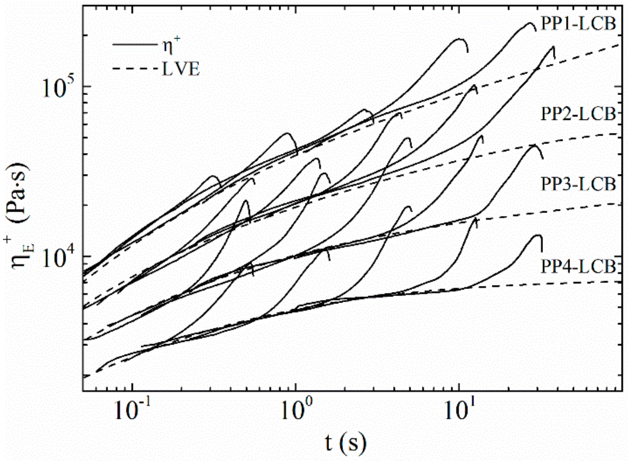

Figure 12. Extensional rheology of the LCB-PPs.

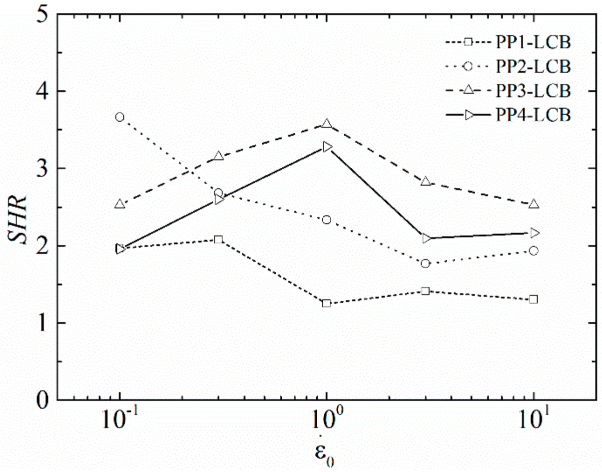

Figure 13. Strain hardening ratio of the LCB samples.

4. Conclusions

In this study a peroxydicarbonate (PODIC) with long aliphatic side chains was used for the LCB of different PP grades. The linear PPs differed in their average molar mass but had similar polydispersity indices. LCB-PPs were prepared via reactive extrusion in melt. The melt viscosity of the LCB-PPs showed classical effects such as an increase in melt elasticity and pronounced strain hardening, which is in agreement with the literature. Furthermore, strain-hardening behaviour was introduced to all LCB-PPs. A strain-hardening dependency of all samples was observed. PP1-LCB and PP2-LCB showed more pronounced strain hardening at low strain rates, which is typical of a low number of branches. LCB was proven by HT-SEC measurements and the deviation of the intrinsic viscosity of the branched samples from their linear PPs was shown. The average branching number per molecule was calculated according to the model of Zimm and Stockmeyer and showed a very low value for PP1-LCB (pipe grade) of 0.08; this value increases to 0.13 for PP2-LCB (from thermoforming grade), and to 0.25 and 0.27 for PP3-LCB (from casting grade) and PP4-LCB (injection moulding grade), respectively. The number average molar mass of PP1-LCB and PP2-LCB decreased compared to their linear feedstocks. Due to the radical reaction mechanism of the LCB, it is suggested that the recombination reaction and therefore the resulting LCB is inhibited by the higher molar mass of PP1. In contrast, the lower molar mass fragments of PP4 lead to a higher number of LCBs. These results will have to be considered for the upcycling of commingled PP single-polymer waste and will be the basis of further studies.

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Author Contributions: Florian Kamleitner designed and performed the experiments analysed the data and wrote the paper. Bernadette Duscher designed the concept of PP up-cycling and analysed the rheological data. Thomas Koch performed the thermal analysis and prepared the graphs. Simone Knaus guided the chemical part of this work. Klaus Schmid gave valuable advice in the mechanism of PODIC assisted long chain branching. Vasiliki-Maria Archodoulaki enabled and guided the project.

Conflicts of Interest: The authors declare no conflict of interest.

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Ausbildung

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Stipendien und Preise

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Sonstiges

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Interessen

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